



Supporting Information

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Synthetic Studies on Tricyclic Diterpenoids: Direct Allylic Amination Reaction of Isopimaric Acid Derivatives**

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SUPPORTING INFORMATION

Table of contents

1. S1. Experimental Section
2. S.1.1. Genaral
3. S1.2. Reactions and synthetic procedures
4. S1.3. Strutures, full chemical names, physical characteristics for synthesized of compounds
5. Table S1. ^{13}C NMR Spectral Data for 4-7, 10-13 (CDCl_3 , δ , ppm)
6. Table S2. ^{13}C NMR Spectral Data for 15, 22-27 (CDCl_3 , δ , ppm)
7. Table S3. ^{13}C NMR Spectral Data for 28-35 (CDCl_3 , δ , ppm)
8. Table S4. ^{13}C NMR Spectral Data for 36, 38-40, 42, 44, 45 (CDCl_3 , δ , ppm)
9. S2. X-ray crystal structure analysis for compounds 5, 24, 27, and 36
10. Table S5. XRD data for compounds 5, 24, 27 and 36
11. Table S6. Parameters of the short inter-molecular and the selected intra-molecular contacts for 24, 27, and 36
12. S3. ^1H and ^{13}C spectra of synthesized compounds.

S1. Experimental Section

S1.1.General: ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker AV-400 (^1H : 400.13 MHz, ^{13}C : 100.78 MHz) or Bruker AV-600 (^1H : 600.30 MHz, ^{13}C : 150.95 MHz) (Bruker BioSpin GmbH, Rheinstetten, Germany) instrument in CDCl_3 , using tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported in ppm downfield from CDCl_3 (δ = 7.27 ppm) for ^1H NMR and relative to the central CDCl_3 resonance (δ = 77.0 ppm) for ^{13}C NMR spectroscopy. In the description of the ^1H and ^{13}C -NMR spectra for compounds **4-7**, **10-13**, **15**, **22-36**, **38-40** **42**, **44**, and **45** the tricyclic diterpenoid core atoms numeration system given in structure **2** was used. The following abbreviations have been used to denote the multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). IR absorption spectra were obtained with a Bruker Vector-22 spectrometer, and values are reported in cm^{-1} . UV spectra were obtained with an HP 8453 UV-Vis spectrometer (Hewlett-Packard, Waldbronn, Germany) in EtOH. HRMS spectra were recorded with a DFS spectrometer (Thermo Scientific, evaporator temperature 240-270°C). The melting points were determined on a Stuart SMF-38 melting point apparatus (Bibby Scientific, Staffordshire, UK) and are uncorrected. Specific rotation $[\alpha]_D$ was measured at room (20-23°C) temperature in CHCl_3 on a Polaar 3005 polarimeter. XRD data for compounds **5**, **24**, **27** were obtained on a Bruker Kappa Apex II CCD diffractometer using φ , ω scans of narrow (0.5°) frames with Mo K α radiation (λ = 0.71073 Å) and a graphite monochromator. The structure was solved by direct methods and refined by full-matrix least-squares method against all F2 in anisotropic approximation using the SHELX-97 programs set.^[24] The hydrogen atoms positions were calculated with the riding model. Absorption corrections were applied using the empirical multiscan method with the SADABS program.^[25] The analytical and spectroscopic investigations were carried out at the Collective Use Center for Chemical Services of the Siberian Branch of the Russian Academy of Sciences.

The reaction progress and the purity of the obtained compounds were monitored by TLC on Silufol UV-254 plates (Kavalier, Czech Republic, CHCl_3 -EtOH, 100:1; detection under UV light or by spraying the plates with 10% water solution of H_2SO_4 followed by heating at 100°C). Column chromatography was performed by using silica gel 60 (0.063–0.200 mm, Merck KGaA, Darmstadt, Germany).

All solvents were freshly distilled under argon prior to being used. Anilines **3,8,9,16-21,37**, benzenesulfonamide (**41**) and *tert*-butyl carbamate (**43**) were commercially obtained from Aldrich and Alpha Aesar. Methyl 14*a*-hydroxy-15,16-dihydroisopimarate (**2**) was prepared according to the literature procedure.^[9]

S1.2. Reactions and synthetic procedures

Reaction of methyl 14 α -hydroxy-15,16-dihydroisopimarate (2) with 2-nitroaniline (3). a) 2-Nitroaniline (3) (410 mg, 3.00 mmol) and AuCl₃ (9 mg, 0.03 mmol) were added to a solution of methyl 14 α -hydroxy-15,16-dihydroisopimarate (2) (500 mg, 1.50 mmol) in CH₃CN (10 mL) under stirring. The mixture was stirred at room temperature for 24 h. Then the solvent was evaporated under reduced pressure, and the residue was subjected to chromatography on silica gel using petroleum ether–ether (10 : 1) as eluent to afford diene **5** as a white solid (9 mg, 2%) and compound **4** as an orange oil (640 mg, 90%). b) 2-Nitroaniline (3) (410 mg, 3.00 mmol) and *p*-toluenesulfonic acid (26 mg, 0.15 mmol) were added to a solution of compound **2** (500 mg, 1.50 mmol) in CH₃CN (10 mL). After stirring for 24 h at room temperature, the solvent was removed in *vacuo* and the residue was subjected to column chromatography on silica gel to afford compounds **5** (114 mg, 24%), **6** as a colorless oil (9 mg, 2%), **4** (164 mg, 24%), and **7** as an orange oil (55 mg, 8%). c) 2-Nitroaniline (3) (410 mg, 3.00 mmol) and BF₃·Et₂O (0.02 ml, 0.15 mmol) were added to a solution of compound **2** (500 mg, 1.50 mmol) in CH₃CN (10 mL). After the stirring for 24 h at room temperature, the solvent was evaporated under reduced pressure, and the residue was subjected to chromatography on silica gel to afford compounds **5** (132 mg, 28%), **6** (28 mg, 6%) and **7** (162 mg, 23%).

Reaction of methyl 14 α -hydroxy-15,16-dihydroisopimarate (2) with 4-nitroaniline (8). 4-Nitroaniline (8) (410 mg, 3.00 mmol) and AuCl₃ (9 mg, 0.03 mmol) were added to a solution of compound **2** (500 mg, 1.50 mmol) in CH₃CN (10 mL) under stirring. The mixture was stirred at 25 °C for 24 h. The solvent was evaporated under reduced pressure, and the residue was subjected to chromatography on silica gel to afford compounds **10** as an yellow oil (533 mg, 74%) and **11** as an yellow oil (142 mg, 19%).

Reaction of methyl 14 α -hydroxy-15,16-dihydroisopimarate (2) with 3-nitroaniline (9). a) 3-Nitroaniline (9) (410 mg, 3.0 mmol) and AuCl₃ (9 mg, 0.03 mmol) were added under stirring to a solution of compound **2** (500 mg, 1.5 mmol) in CH₃CN (10 mL). After the stirring for 24 h at room temperature, the solvent was evaporated under reduced pressure, and the residue was subjected to column chromatography on silica gel to afford compounds **12** as an orange oil (160 mg, 24%), **13** as an yellow oil (40 mg, 6%), **15** as an orange oil (88 mg, 13%), **14** as a white solid (93 mg, 14%), and **2** (120 mg, 24%). b) 3-Nitroaniline (9) (410 mg, 3.0 mmol) and AuCl₃ (27 mg, 0.09 mmol) were added under stirring to a solution of compound **2** (500 mg, 1.5 mmol) in CH₃CN (10 mL). After the stirring for 24 h at room temperature, the solvent was evaporated under reduced pressure, and the residue was subjected to column chromatography on silica gel in the mentioned conditions to afford compounds **12** (354 mg, 52%), **13** (73 mg, 11%), **15** (149 mg, 22%), **14** (33 mg, 5%), and **2** (40 mg, 8%). c) Methyl 14 α -hydroxy-15,16-dihydroisopimarate **2** (500 mg, 1.5 mmol) was dissolved in CH₃CN (10 mL) and 3-nitroaniline (9) (410 mg, 3.0 mmol), AuCl₃ (9 mg, 0.03 mmol), AgOTf (23 mg, 0.09 mmol) were added in succession under stirring. The mixture was stirred for 24 h at room temperature, the solvent was evaporated under reduced pressure, and the residue was subjected to chromatography on silica gel to afford compounds **12** (347 mg, 51%), **13** (53 mg, 8%), **15** (125 mg, 18%), **14** (60 mg, 9%), and **2** (40 mg, 8%). d) Compound **2** (500 mg, 1.5 mmol) was dissolved in CH₃NO₂ (5 mL) and 3-nitroaniline (9) (410 mg, 3.00 mmol), AuCl₃ (9 mg, 0.03 mmol) and AgOTf (23 mg, 0.09 mmol) were added in succession under stirring. After stirring for 24 h at room temperature, the solvent was removed in *vacuo* and the residue was subjected to column chromatography on silica gel to afford compounds **12** (428 mg, 63%), **13** (59 mg, 9%), and **15** (132 mg, 19%). e) 3-Nitroaniline (9) (410 mg, 3.00 mmol) and AgOTf (23 mg, 0.09 mmol) were added to a solution of compound **2** (500 mg, 1.50 mmol) in CH₃NO₂ (5 mL). After the stirring for 24 h at room temperature, the solvent was evaporated under reduced pressure, and the residue was subjected to column chromatography on silica gel to afford compounds **12** (307 mg, 45%), **13** (46 mg, 7%), **15** (105 mg, 16%), **14** (112 mg, 13%), and **2** (65 mg, 13%). f) 3-Nitroaniline (9) (410 mg, 3.0 mmol) and AgBF₄ (12 mg, 0.06 mmol) were added to a solution of compound **2** (500 mg, 1.5 mmol) in CH₃CN (10 mL). After stirring for 24 h at room temperature, the solvent was evaporated under reduced pressure, and the residue was subjected to column chromatography on silica gel to afford compounds **12** (230 mg, 34%), **13** (27 mg, 4%), **15** (81 mg, 12%), **14** (40 mg, 8%), and **2** (190 mg, 38%). g) 3-Nitroaniline (9) (410 mg, 3.0 mmol), AuCIPPh₃ (26 mg, 0.03 mmol) and AgBF₄ (12 mg, 0.06 mmol) were successfully added to a stirring solution of compound **2** (500 mg, 1.5 mmol) in CH₃CN (10 mL). After stirring for 24 h at room temperature, the solvent was evaporated under reduced pressure, and the residue was subjected to column chromatography to afford compounds **12** (290 mg, 38%), **13** (28 mg, 8%), **15** (102 mg, 15%), **14** (70 mg, 14%), and **2** (115 mg, 23%). h) Compound **2** (500 mg, 1.5 mmol) was dissolved in CH₃CN (10 mL) and 3-nitroaniline (9) (410 mg, 3.0 mmol), AuCIPPh₃ (26 mg, 0.03 mmol) and AgOTf (11 mg, 0.03 mmol) were added under stirring. The mixture was stirred for 24 h at room temperature, then the solvent was removed in *vacuo*, and the residue was subjected to column chromatography to afford compounds **12** (217 mg, 32%), **13** (34 mg, 5%), **15** (82 mg, 12%), **14** (75 mg, 15%), and **2** (100 mg, 20%). i) 3-Nitroaniline (9) (410 mg, 3.00 mmol), AuCIPPh₃ (26 mg, 0.03 mmol) and AgOTf (23 mg, 0.09 mmol) were added in succession to a stirred solution of compound **2** (500 mg, 1.5 mmol) in CH₃CN (10 mL). The mixture was stirred for 24 h, then the solvent was removed under reduced pressure, and the residue was subjected to column chromatography to afford compounds **12** (279 mg, 41%), **13** (60 mg, 9%), **15** (111 mg, 16%), **14** (40 mg, 6%), and **2** (20 mg, 4%).

Reaction of methyl 14 α -hydroxy-15,16-dihydroisopimarate (2) with 2-bromoaniline (16). a) Compound **2** (500 mg, 1.5 mmol) was dissolved in CH₃NO₂ (5 mL) and 2-bromoaniline (**16**) (380 mg, 3.0 mmol), AuCl₃ (9 mg, 0.03 mmol) and AgOTf (23 mg, 0.09 mmol) were added in succession under stirring. The mixture was stirred for 24 h at room temperature, the solvent was evaporated under reduced pressure, and the residue was subjected to column chromatography on silica gel to afford compounds **22** as a colorless oil (388 mg, 53%), **28** as a colorless oil (73 mg, 10%), and **29** as a colorless oil (44 mg, 6%). b) To a stirring solution of compound **2** (500 mg, 1.5 mmol) in CH₃CN (10 mL) 2-bromoaniline **16** (380 mg, 3.0 mmol), AuCl₃ (9 mg, 0.03 mmol) and AgOTf (23 mg, 0.09 mmol) were added in succession under. The mixture was stirred for 24 h at room temperature, then the solvent was removed in *vacuo*, and the residue was subjected to column chromatography on silica gel to afford compounds **5** (10 mg, 2%), **6** (5 mg, 1%), **22** (284 mg, 39%), **30** as a colorless oil (139 mg, 19%), **31** as a colorless oil (117 mg, 16%), **14** (65 mg, 13%), and **2** (50 mg).

(1*R*,4*aR*,4*b**R*,7*S*,9*R*,10*a**R*)-Methyl 9-((2-chloro-4-nitrophenyl)amino)-7-ethyl-1,4*a*,7-trimethyl-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenan-threne-1-carboxylate (23).** Compound **2** (500 mg, 1.5 mmol) was dissolved in CH₃CN (10 mL) and 2-chloro-4-nitroaniline (**17**) (520 mg, 3.0 mmol), AuCl₃ (9 mg, 0.03 mmol), and AgOTf (23 mg, 0.09 mmol) were added in succession under stirring. The mixture was stirred for 24 h at room temperature, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel to afford diene **6** (66 mg, 14%) and compound **23** as a yellow oil (381 mg, 52%).

(1*R*,4*aR*,4*b**R*,7*S*,9*R*,10*a**R*)-Methyl 7-ethyl-9-((4-methoxy-2-nitrophenyl)-amino)-1,4*a*,7-trimethyl-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenan-threne-1-carboxylate (24).** Compound **2** (500 mg, 1.5 mmol) was dissolved in CH₃CN (10 mL) and 4-methoxy-2-nitroaniline (**18**) (504 mg, 3.0 mmol), AuCl₃ (9 mg, 0.03 mmol) and AgOTf (23 mg, 0.09 mmol) were added in succession under stirring. The mixture was stirred for 24 h at room temperature, the solvent was removed under reduced pressure, and the residue was subjected to chromatography on silica gel to afford dienes **5** (24 mg, 5%), **6** (14 mg, 3%), and compound **24** as a red powder (589 mg, 81%).

(1*R*,4*aR*,4*b**R*,7*S*,9*R*,10*a**R*)-Methyl 7-ethyl-1,4*a*,7-trimethyl-9-((3-(trifluoromethyl)phenyl)amino)-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydro-phenanthrene-1-carboxylate (25).** To a stirred solution of compound **2** (500 mg, 1.5 mmol) and 3-(trifluoromethyl)aniline (**18**) (483 mg, 3.0 mmol) in CH₃NO₂ (5 mL) AuCl₃ (9 mg, 0.03 mmol), and AgOTf (23 mg, 0.09 mmol) were added. The mixture was stirred for 24 h at room temperature, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel to afford compounds **5** (9 mg, 2%), **6** (9 mg, 2%), **25** as a colorless oil (343 mg, 48%), **33** as a pale yellow oil (93 mg, 13%), and **32** as a pale yellow oil (143 mg, 20%).

(1*R*,4*aR*,4*b**R*,7*S*,9*R*,10*a**R*)-Methyl 7-ethyl-1,4*a*,7-trimethyl-9-((4-(trifluoromethyl)phenyl)-amino)-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodeca-hydrophenanthrene-1-carboxylate (26).** Compound **2** (500 mg, 1.5 mmol) was dissolved in CH₃CN (10 mL) and 4-(trifluoromethyl)aniline **20** (483 mg, 3.0 mmol), AuCl₃ (9 mg, 0.03 mmol), and AgOTf (23 mg, 0.09 mmol) were added in succession under stirring. The mixture was stirred for 24 h at room temperature, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel to afford compounds **26** as a pale yellow oil (501 mg, 70%), **35** (100 mg, 14%), **34** as a pale yellow oil (100 mg, 14%), and **14** (30 mg, 6%).

(1*R*,4*aR*,4*b**R*,7*S*,9*R*,10*a**R*)-Methyl 9-((4-acetylphenyl)amino)-7-ethyl-1,4*a*,7-trimethyl-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (27).** Compound **2** (500 mg, 1.5 mmol) was dissolved in CH₃NO₂ (5 mL) and 1-(4-aminophenyl)ethanone **21** (400 mg, 3.0 mmol), AuCl₃ (9 mg, 0.03 mmol), and AgOTf (23 mg, 0.09 mmol) were added in succession under stirring. The mixture was stirred at 25 °C for 24 h. The solvent was distilled off under reduced pressure, and the residue was subjected to column chromatography on silica gel to afford compounds **27** as an orange oil (454 mg, 67%) and **36** (76 mg, 11%).

(1*R*,4*aR*,4*b**R*,7*S*,9*S*,10*a**R*)-Methyl 7-ethyl-1,4*a*,7-trimethyl-9-(methyl(4-nitrophenyl)-amino)-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenan-threne-1-carboxylate (38).** Compound **2** (500 mg, 1.5 mmol) was dissolved in CH₃CN (10 mL) and N-methyl-4-nitroaniline (**37**) (456 mg, 3.00 mmol), AuCl₃ (9 mg, 0.03 mmol), and AgOTf (23 mg, 0.09 mmol) were added in succession under stirring. The mixture was stirred for 24 h at room temperature, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography to afford compounds **5** (149 mg, 31%), **6** (14 mg, 3%), **38** as an yellow oil (126 mg, 18%), and **39** as a colorless oil (148 mg, 15%).

(1*R*,4*aR*,4*b**R*,7*S*,9*S*,10*a**R*)-Methyl 7-ethyl-1,4*a*,7-trimethyl-9-((4-nitrophenyl)amino)-1,2,3,4, 4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (40).** Dimer **39** (500 mg, 0.77 mmol) was dissolved in CH₃NO₂ (5 mL) and 4-nitroaniline (**8**) (212 mg, 1.54 mmol), AuCl₃ (5 mg, 0.02 mmol), and AgOTf (11 mg, 0.05 mmol) were added in succession under stirring. The mixture was stirred for 24 h at room temperature, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography to afford compounds **5** (185 mg, 38%), **10** (160 mg, 23%), and **40** as an yellow oil (160 mg, 23%).

(1*R*,4*aR*,4*b**R*,7*S*,9*R*,10*a**R*)-Methyl 7-ethyl-1,4*a*,7-trimethyl-9-(phenyl-sulfonamido)-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (42).** Compound **2** (500 mg, 1.50 mmol) was dissolved in CH₃CN (10 mL) and benzenesulfonamide (**41**) (472 mg, 3.00 mmol), AuCl₃ (5 mg, 0.02 mmol), and AgOTf (11 mg, 0.05 mmol) were added in succession under stirring. The mixture was stirred for 24 h at room temperature, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel to afford compounds **5** (57 mg, 12%), **6** (28 mg, 6%), and **42** as a white solid (291 mg, 41%).

(1*R*,4*aR*,4*b**R*,7*S*,9*R*,10*a**R*)-Methyl 9-((tert-butoxycarbonyl)amino)-7-ethyl-1,4*a*,7-trimethyl-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (44).** Compound **2** (500 mg, 1.5 mmol) was dissolved in CH₃NO₂ (5 mL) and *tert*-butyl carbamate (**43**) (351 mg, 3.00 mmol), AuCl₃ (9 mg, 0.03 mmol), and AgOTf (23 mg, 0.09 mmol) were added in succession under stirring. The mixture was stirred for 24 h at room temperature, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel to afford compound **44** as a colorless oil (422 mg, 65%).

(1*R*,4*aR*,4*b**R*,7*S*,9*R*,10*a**R*)-Methyl 9-amino-7-ethyl-1,4*a*,7-trimethyl-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (45).** Compound **44** (500 mg, 1.5 mmol) was dissolved in CH₃OH (10 mL) and 1.5 mL of concentrated HCl was added under stirring at 20°C and the mixture was left to stand for 24 h at 20°C, then treatment by adding of 0.5 mL of triethylamine. The solvent was evaporated under reduced pressure. Water (5 mL) was added

and extractions with CH_2Cl_2 (4×10 mL) was performed. The combined organic layers were dried with magnesium sulfate, filtrated and concentrated in vacuo. The oily residue was purified by column chromatography on silica gel using petroleum ether-methanol (10 : 1) as an eluent, to afford compound **45** as a colorless oil (450 mg, 90%).

Treatment of 2 with AuCl_3 in CH_3CN . A solution of compound **2** (500 mg, 1.5 mmol) in CH_3CN (10 mL) was treated by AuCl_3 (9 mg, 0.03 mmol). After stirring of the mixture for 24 h at ambient temperature, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel to afford compounds **5** (50 mg, 8%), **39** (148 mg, 15%), **14** (140 mg, 28%), and **2** (180 mg).

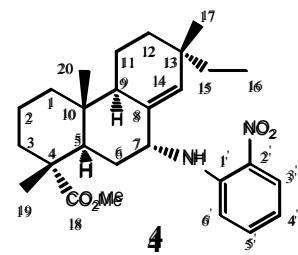
Treatment of 2 with $\text{AuCl}_3\text{-AgOTf}$ in CH_3NO_2 . Compound **2** (500 mg, 1.50 mmol) was dissolved in CH_3NO_2 (5 mL) and AuCl_3 (9 mg, 0.03 mmol) and AgOTf (23 mg, 0.09 mmol) were added under stirring. The mixture was stirred for 24 h at room temperature, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography to afford dienes **5** (144 mg, 23%), **6** (325 mg, 69%) and starting compound **2** (11 mg).

Reaction of methyl 7 α -hydroxy-15,16-dihydrosandaracopimorate (14) with 3-nitroaniline (9). Compound **14** (500 mg, 1.50 mmol) was dissolved in CH_3NO_2 (5 mL) and 3-nitroaniline (**9**) (410 mg, 3.00 mmol), AuCl_3 (9 mg, 0.03 mmol), and AgOTf (23 mg, 0.09 mmol) were added in succession under stirring. The mixture was stirred for 24 h at room temperature, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography to afford compounds **12** (347 mg, 51%), **13** (46 mg, 7%), **15** (105 mg, 15%), and **14** (100 mg, 13%).

X-ray crystal structure analysis for compounds 5, 24, 27, and 36: The compounds **24**, **27** crystallizes in the orthorhombic space groups $P2_12_12_1$, while **5**, **36** crystallizes in the monoclinic $P2_1$ group. The crystallographic data are listed in Table S5. Molecular structure of compounds **6**, **24**, **27**, **36** is illustrated in Fig. 2. The obtained crystal structures were analyzed for short contacts between non-bonded atoms using PLATON [26] and MERCURY programs [27]. CCDC 1407201 (**5**), 1407203 (**24**), 1407202 (**27**), 1422327 (**36**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

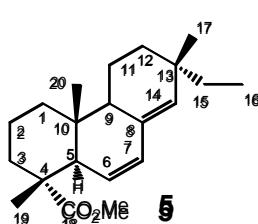
S1.3. S1.3. Structures, full chemical names, physical characteristics for synthesized compounds

(1*R*,4*aR*,4*bR*,7*S*,9*R*,10*aR*)-Methyl 7-ethyl-1,4*a*,7-trimethyl-9-[(2-nitro-phenyl)amino]-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydronanthrene-1-carboxylate (**4**).



$R_f = 0.60$ (CHCl_3); $[\alpha]_D = -40.8$ ($c = 6.0$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3): $\delta = 0.74$ (t, $J = 7.4$ Hz, 3 H, CH_3 -16), 0.87 (s, 3 H, CH_3 -20), 0.92 (s, 3 H, CH_3 -17), 1.18-1.28 (m, 2 H, H-1,12), 1.20 (s, 3 H, CH_3 -19), 1.23 (m, 2 H, CH_2 -15), 1.30 (m, 1 H, H-12), 1.46 (m, $J_{\text{gem}} = 13.5$ Hz, 1 H, H-6), 1.52-1.58 (m, 4 H, CH_2 -2, CH_2 -11), 1.62 (m, 1 H, H-3), 1.72 (m, 1 H, H-3), 1.78 (m, 1 H, H-1), 1.79 (ddd, $J_{\text{gem}} = 13.5$, $J = 12.0$, 3.8 Hz, 1 H, H-6), 2.08 (dd, $J = 8.6$, 1.8 Hz, 1 H, H-9), 2.33 (dd, $J = 12.0$, 1.8 Hz, 1 H, H-5), 3.36 (s, 3 H, OCH_3), 4.16 (brd, $J_{\text{H7-NH}} = 6.0$ Hz, 1 H, H^b-7), 5.59 (brs, 1 H, H-14), 6.56 (t, $J = 8.5$ Hz, 1 H, H-4'), 6.89 (d, $J = 8.5$ Hz, 1 H, H-6'), 7.35 (t, $J = 8.5$ Hz, 1 H, H-5'), 8.14 (d, $J = 8.5$ Hz, 1 H, H-3'), 8.48 (d, $J = 6.0$ Hz, 1 H, NH). $^{13}\text{C NMR}$ (151 MHz, CDCl_3): see Table S1. IR (neat): $\nu = 746, 1035, 1145, 1190, 1244, 1259, 1278, 1338, 1352, 1419, 1444, 1460, 1506, 1571, 1616, 1724, 2848, 2868, 2925, 2949$ cm⁻¹. UV (EtOH) λ_{max} nm (lg ϵ): 236 (3.99), 282 (4.22), 434 (3.40). MS (EI): m/z (%) = 454 (9) [M⁺], 317 (39), 287 (23), 257 (100), 227 (12), 145 (11), 121 (20), 105 (11), 95 (11), 84 (16), 82 (25), 57 (13); calcd. for $\text{C}_{27}\text{H}_{38}\text{O}_4\text{N}_2$: 454.2826, found 454.2829.

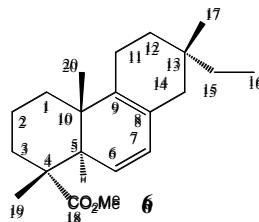
(1*R*,4*aR*,4*bR*,7*S*,10*aR*)-Methyl 7-ethyl-1,4*a*,7-trimethyl-1,2,3,4,4*a*,4*b*,5,6,7,10*a*-decahydronanthrene-1-carboxylate (**5**).



Compound **5** was crystallized from MeOH, m.p. 58-60°C. $R_f = 0.66$ (CHCl_3); $[\alpha]_D = +23.81$ ($c = 0.2$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3): $\delta = 0.72$ (s, 3 H, CH_3 -20), 0.79 (t, $J = 7.5$ Hz, 3 H, CH_3 -16), 0.91 (s, 3 H, CH_3 -17), 1.12 (dd, $J = 12.8$, 4.0 Hz, 1 H, H-1), 1.19 (s, 3 H, CH_3 -19), 1.27 (m, 2 H, CH_2 -15), 1.35 (m, 2 H, H-12,11), 1.39 (m, 1 H, H-3), 1.72 (m, 1 H, H-3), 1.78 (m, 1 H, H-1), 1.82 (d, $J = 8.5$ Hz, 1 H, H-6), 2.08 (dd, $J = 8.6$, 1.8 Hz, 1 H, H-9), 2.33 (dd, $J = 12.0$, 1.8 Hz, 1 H, H-5), 3.36 (s, 3 H, OCH_3), 4.16 (brd, $J_{\text{H7-NH}} = 6.0$ Hz, 1 H, H^b-7), 5.59 (brs, 1 H, H-14), 6.56 (t, $J = 8.5$ Hz, 1 H, H-4'), 6.89 (d, $J = 8.5$ Hz, 1 H, H-6'), 7.35 (t, $J = 8.5$ Hz, 1 H, H-5'), 8.14 (d, $J = 8.5$ Hz, 1 H, H-3'), 8.48 (d, $J = 6.0$ Hz, 1 H, NH). $^{13}\text{C NMR}$ (151 MHz, CDCl_3): see Table S1. IR (neat): $\nu = 746, 1035, 1145, 1190, 1244, 1259, 1278, 1338, 1352, 1419, 1444, 1460, 1506, 1571, 1616, 1724, 2848, 2868, 2925, 2949$ cm⁻¹. UV (EtOH) λ_{max} nm (lg ϵ): 236 (3.99), 282 (4.22), 434 (3.40). MS (EI): m/z (%) = 454 (9)

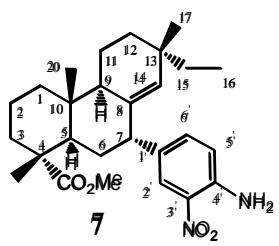
12), 1.48-1.61 (m, 3 H, H-2,11,3), 1.64 (m, 1 H, H-2), 1.70 (m, J_{gem} = 12.8 Hz, 1 H, H-1), 1.74 (m, 1 H, H-3), 2.01 (m, 1 H, H-9), 2.69 (s, 1 H, H-5), 3.65 (s, 3 H, OCH₃), 5.25 (m, 2 H, H-6,14), 5.95 (dd, J = 9.8, 2.9 Hz, 1 H, H-7). ¹³C NMR (151 MHz, CDCl₃): see Table S1. IR (neat): ν = 1112, 1149, 1188, 1244, 1384, 1434, 1460, 1616, 1728, 2850, 2866, 2935, 3012 cm⁻¹. UV (EtOH) λ_{max} nm (lg ϵ): 236 (4.23), 242 (4.25). MS (EI): *m/z* (%) = 316 (42), 288 (22), 287 (100), 256 (26), 241 (28), 227 (60), 145 (39), 105 (22), 95 (23), 55 (10); calcd. for C₂₁H₃₂O₂: 316.2397, found 316.2392.

(1*R*,4*aS*,7*S*,10*aR*)-Methyl 7-ethyl-1,4*a*,7-trimethyl-1,2,3,4,4*a*,5,6,7,8,10*a*-decahydronaphthalene-1-carboxylate (6).



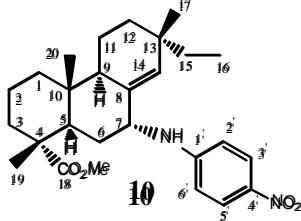
R_f = 0.66 (CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.77 (t, J = 7.5 Hz, 3 H, CH₃-16), 0.78 (s, 3 H, CH₃-20), 0.96 (s, 3 H, CH₃-17), 1.14-1.25 (m, 3 H, CH₂-15, H-1), 1.23 (s, 3 H, CH₃-19), 1.40 (m, 2 H, CH₂-12), 1.55-1.62 (m, 3 H, CH₂-2, H-3), 1.72 (m, 2 H, H-1,3), 1.84-1.97 (m, 4 H, CH₂-14,11), 3.61 (s, 3 H, OCH₃), 3.65 m, 1 H, H-5), 5.33 (m, 2 H, H-6,7). ¹³C NMR (101 MHz, CDCl₃): see Table S1. IR (neat): ν = 866, 1149, 1244, 1384, 1433, 1460, 1616, 1728, 2850, 2866, 2925 cm⁻¹. UV (EtOH) λ_{max} nm (lg ϵ): 241 (3.92). MS (EI): *m/z* (%) = 316.2 (2), 241 (2), 87 (10), 85 (66), 83 (100) 50 (7), 48 (11), 47 (22), 35 (10); calcd. for C₂₁H₃₂O₂: 316.2397, found 316.2393.

(1*R*,4*aR*,4*bR*,7*S*,9*S*,10*aR*)-Methyl 9-(4-amino-3-nitrophenyl)-7-ethyl-1,4*a*,7-trimethyl-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydronaphthalene-1-carboxylate (7).



R_f = 0.44 (CHCl₃); $[\alpha]_D$ = -43.3 (c 6.0, CHCl₃); ¹H NMR (600 MHz, CDCl₃): δ = 0.84 (t, J = 7.3 Hz, 3 H, CH₃-16), 0.89 (s, 3 H, CH₃-20), 0.95 (s, 3 H, CH₃-17), 1.03 (m, 1 H, H-1), 1.21 (s, 3 H, CH₃-19), 1.34 (m, 2 H, CH₂-15), 1.40 (m, 2 H, CH₂-12), 1.49 (m, 3 H, H-2,11,3), 1.63 (m, 3 H, H-2,11,6), 1.67 (m, 2 H, H-3,1), 1.74 (dd, J = 12.6, 2.0 Hz, 1 H, H-5), 1.88 (m, 1 H, H-9), 1.94 (ddd, J = 13.0, 12.5, 5.4 Hz, 1 H, H-6), 3.40 (d, J = 5.4 Hz, 1 H, H-7), 3.52 (s, 3 H, OCH₃), 5.42 (s, 1 H, H-14), 5.95 (brs, 2 H, NH₂), 6.72 (d, J = 8.7 Hz, 1 H, H-5'), 7.26 (dd, J = 8.7, 1.8 Hz, 1 H, H-6'), 8.01 (d, J = 1.8 Hz, 1 H, H-2'). ¹³C NMR (151 MHz, CDCl₃): see Table S1 (Supp. Info). IR (neat): ν = 758, 1099, 1143, 1172, 1188, 1252, 1340, 1387, 1407, 1460, 1517, 1562, 1591, 1633, 1724, 2850, 2869, 2945, 3489, 3365, 3489 cm⁻¹. UV (EtOH) λ_{max} nm (lg ϵ): 236 (4.3), 281 (3.7), 420 (2.5). MS (EI): *m/z* (%) = 454 (100), 454 (100), 426 (18), 425 (60), 365 (69), 287 (40), 227 (29), 151 (55), 121 (41), 95 (29), 85 (29), 83 (45); calcd. for C₂₇H₃₈O₄N₂: 454.2829, found 454.2821.

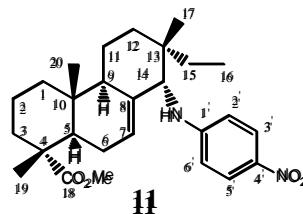
(1*R*,4*aR*,4*bR*,7*S*,9*R*,10*aR*)-Methyl 7-ethyl-1,4*a*,7-trimethyl-9-[(4-nitro-phenyl)amino]-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydronaphthalene-1-carboxylate (10).



R_f = 0.66 (CHCl₃); $[\alpha]_D$ = +54 (c 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.78 (t, J = 7.2 Hz, 3 H, CH₃-16), 0.86 (s, 3 H, CH₃-20), 0.92 (s, 3 H, CH₃-17), 1.18 (m, 2 H, H-1,12), 1.21 (s, 3 H, CH₃-19), 1.25 (m, 2 H, CH₂-15), 1.31 (m, 1 H, H-12), 1.43 (m, 1 H, H-6), 1.55, 1.59, 1.62, 1.66 (all m, 6 H, CH₂-2,11,3), 1.75 (m, 1 H, H-1), 1.77 (ddd, J = 13.4, 12.4, 4.2 Hz, 1 H, H-6), 2.02 (m, 1 H, H-9), 2.25 (dd, J = 12.4, 1.6 Hz, 1 H, H-5), 3.45 (s, 3 H, OCH₃), 4.00 (dd, J = 4.2, 6.0 Hz, 1 H, H-7), 4.97 (d, J = 6.0 Hz, 1 H, NH), 5.62 (s, 1 H, H-14), 6.56 (d, J = 8.6 Hz, 2 H, H-2',6'), 8.04 (d, J = 8.6 Hz, 2 H, H-3',5'). ¹³C NMR (101 MHz, CDCl₃): see Table S1. IR (neat): ν = 833, 1065, 1084, 1111, 1188, 1242, 1275, 1320, 1474, 1504, 1526, 1599, 1726, 2853, 2945, 3385 cm⁻¹. UV (EtOH) λ_{max} nm (lg ϵ): 235 (3.91), 394 (4.32). MS (EI): *m/z* (%) = 454 (8) [M]⁺,

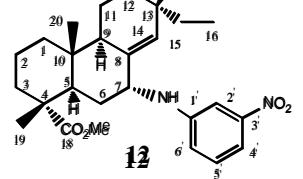
318 (8), 317 (34), 287 (9), 285 (7), 258 (23), 257 (100), 227 (6), 201 (6), 173 (7), 159 (5), 147 (5), 145 (7), 135 (6), 133 (6), 131 (4), 123 (5), 121 (29), 119 (7), 109 (6), 108 (9), 107 (8), 105 (11), 95 (8), 93 (9), 91 (8), 81 (7), 79 (7), 77 (3), 69 (4), 67 (5), 55 (9), 41 (6). HRMS calcd. for $C_{27}H_{38}O_4N_2$: 454.2826, found 454.2818

(1*R*,4*aR*,4*bR*,7*S*,8*S*,10*aR*) Methyl 7-ethyl-1,4*a*,7-trimethyl-8-((4-nitro-phenyl)amino)-1,2,3,4,4*a*,4*b*,5,6,7,8,10,10*a*-dodecahydrophenanthrene-1-carboxylate (11).

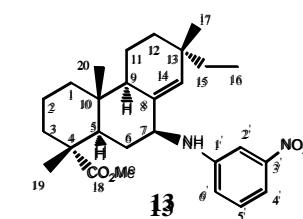


$R_f = 0.66$ ($CHCl_3$); $[\alpha]_D = + 254$ (c 0.2, $CHCl_3$); 1H NMR (600 MHz, $CDCl_3$): $\delta = 0.74$ (t, $J = 7.5$ Hz, 3 H, CH_3 -16), 0.86 (s, 3 H, CH_3 -17), 0.89 (s, 3 H, CH_3 -20), 1.06 (m, 1 H, H-1), 1.22 (s, 3 H, CH_3 -19), 1.29 (m, 2 H, H-15), 1.36-1.46 (m, 4 H, CH_2 -12, H-11,2), 1.50-1.61 (m, 6 H, CH_2 -6,3, H-2,11), 1.73 (dd, $J = 12.1$, 4.0 Hz, 1 H, H-5), 1.82 (m, J_{gem} = 12.9 Hz, 1 H, H-1), 1.97 (m, 1 H, H-9), 3.54 (s, 3 H, OCH_3), 3.57 (brd, $J = 5.6$ Hz, 1 H, H-14), 4.60 (d, $J = 5.6$ Hz, 1 H, NH), 5.61 (d, $J = 5.9$ Hz, 1 H, H-7), 6.53 (d, $J = 8.6$ Hz, 2 H, H-2',6'), 8.03 (d, $J = 8.6$ Hz, 2 H, H-3',5'). ^{13}C NMR (151 MHz, $CDCl_3$): see Table S1. IR (neat): $\nu = 754, 833, 1065, 1111, 1146, 1188, 1246, 1267, 1308, 1435, 1474, 1503, 1531, 1599, 1711, 1722, 2855, 2870, 2928, 3379$ cm $^{-1}$. UV (EtOH) λ_{max} nm (lg ϵ): 235 (3.9), 396 (4.2). MS (EI): m/z (%) = 454 (15) [M^+], 318 (13), 317 (57), 287 (13), 258 (23), 257 (100), 227 (7), 225 (7), 173 (8), 145 (8), 121 (20), 119 (10), 105 (10), 95 (7), 93 (7), 91 (8), 55 (11), 41 (6); calcd. for $C_{27}H_{38}O_4N_2$: 454.2827, found 454.2818.

(1*R*,4*aR*,4*bR*,7*S*,9*R*,10*aR*)-Methyl 7-ethyl-1,4*a*,7-trimethyl-9-((3-nitrophe-nyl)amino)-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (12).



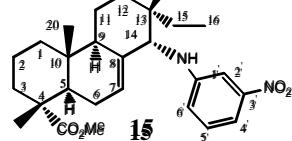
$R_f = 0.62$ ($CHCl_3$); $[\alpha]_D = + 8.56$ (c 7.8, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$): $\delta = 0.73$ (t, $J = 7.5$ Hz, 3 H, CH_3 -16), 0.86 (s, 3 H, CH_3 -20), 0.90 (s, 3 H, CH_3 -17), 1.16 (m, 2 H, H-1,12), 1.21 (s, 3 H, CH_3 -19), 1.24 (m, 2 H, CH_2 -15), 1.31 (m, 1 H, H-12), 1.43 (m, 1 H, H-6), 1.52-1.60 (m, 4 H, CH_2 -2,11), 1.65 (m, 2 H, CH_2 -3), 1.74 (m, 1 H, H-1), 1.78 (ddd, $J = 13.2$, 12.2, 4.0 Hz, 1 H, H-6), 2.02 (m, 1 H, H-9), 2.28 (dd, $J = 12.2$, 2.2 Hz, 1 H, H-5), 3.47 (s, 3 H, OCH_3), 3.93 (dd, $J = 5.6$, 3.4, 1 H, H-7), 5.63 (s, 1 H, H-14), 6.88 (d, $J = 8.3$ Hz, 1 H, H-6'), 7.21 (t, $J = 8.3$ Hz, 1 H, H-5'), 7.44 (m, 3 H, H-2',4',NH). ^{13}C NMR (101 MHz, $CDCl_3$): see Table S1. IR (neat): $\nu = 734, 758, 825, 1060, 1080, 1095, 1122, 1132, 1145, 1190, 1215, 1247, 1348, 1384, 1433, 1446, 1460, 1485, 1529, 1581, 1622, 1724, 2852, 2868, 2931, 2947, 3402$ cm $^{-1}$. UV (EtOH) λ_{max} nm (lg ϵ): 191 (3.36), 196 (3.61), 248 (4.02). MS (EI): m/z (%) = 454 (11), 317 (40), 257 (100), 121 (30), 55 (58), 43 (42), 41 (82), 29 (54), 15 (25); calcd. for $C_{27}H_{38}O_4N_2$: 454.2826, found 454.2822.



(1*R*,4*aR*,4*bR*,7*S*,9*S*,10*aR*)-Methyl 7-ethyl-1,4*a*,7-trimethyl-9-((3-nitrophe-nyl)amino)-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (13). $R_f = 0.62$ ($CHCl_3$); 1H NMR (600 MHz, $CDCl_3$): $\delta = 0.61$ (t, $J = 7.5$ Hz, 3 H, CH_3 -16), 0.83 (s, 3 H, CH_3 -20), 0.85 (s, 3 H, CH_3 -17), 1.13-1.22 (m, 3 H, CH_2 -15, H-1), 1.20 (s, 3 H, CH_3 -19), 1.28 (m, 2 H, CH_2 -12), 1.38-1.45 (m, 1 H, H-6), 1.49 (m, 1 H, H-11), 1.52-1.67 (m, 3 H, CH_2 -2, H-6), 1.61 (m, 1 H, H-3), 1.67 (m, 1 H, H-11), 1.74 (m, 2 H, H-1,3), 1.90 (m, 1 H, H-9), 2.07 (dd, $J = 12.4$, 2.4 Hz, 1 H, H-5), 3.64 (s, 3 H, OCH_3), 3.75 (ddd, $J = 12.0$, 5.6, 2.3 Hz, 1 H, H-7), 4.03 (d, $J = 5.6$ Hz, 1 H, NH), 5.34 (s, 1 H, H-14), 6.78 (dd, $J = 8.1$, 2.1 Hz, 1 H, H-6'), 7.21 (t, $J = 8.1$ Hz, 1 H, H-5'), 7.29 (t, $J = 2.1$ Hz, 1 H, H-2'), 7.44 (dd, $J = 8.1$, 2.1 Hz, 1 H, H-4'). ^{13}C NMR (151 MHz, $CDCl_3$): see Table S1. IR (neat): $\nu = 723, 741, 822, 1047, 1060, 1099, 1132, 1146, 1184, 1244, 1280, 1350, 1385, 1460, 1531, 1539, 1620, 1726, 2853, 2866, 2928, 2949, 3399$ cm $^{-1}$. UV (EtOH) λ_{max} nm (lg ϵ): 246 (4.3), 405 (3.1). MS (EI): m/z (%) = 454 (3), 425 (15), 329 (13), 318 (16), 317 (73), 287 (13), 286 (66), 285 (22), 269 (14), 258 (23), 257 (100),

207 (10), 181 (9), 173 (11), 149 (8), 147 (9), 145 (10), 121 (25), 119 (8), 109 (8), 105 (10), 95 (13), 93 (8), 91 (9), 81 (11), 55 (7), 41 (5); calcd. for C₂₇H₃₈O₄N₂: 454.2826, found 454.2820.

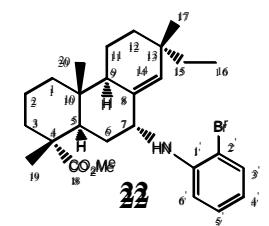
(1*R*,4*aR*,4*bR*,7*S*,8*S*,10*aR*)-Methyl 7-ethyl-1,4*a*,7-trimethyl-8-((3-nitrophenyl)amino)-1,2,3,4,4*a*,4*b*,5,6,7,8,10,10*a*-dodecahydrophenanthrene-1-carboxylate (15).



R_f = 0.62 (CHCl₃); $[\alpha]_D$ = -138.55 (c 0.2, CHCl₃); ¹H NMR (600 MHz, CDCl₃): δ = 0.77 (t, J = 7.4 Hz, 3 H, CH₃-16), 0.86 (s, 3 H, CH₃-17), 0.88 (s, 3 H, CH₃-20), 1.07 (m, 1 H, H-1), 1.21 (s, 3 H, CH₃-19), 1.24-1.32 (m, 2 H, H-15), 1.35-1.44 (m, 4 H, CH₂-12, H-11,2), 1.48-1.65 (m, 6 H, CH₂-6,3, H-2,11), 1.70 (dd, J = 12.0, 3.0 Hz, 1H, H-5), 1.81 (m, J_{gem} = 13.2 Hz, 1 H, H-1), 1.88 (m, 1 H, H-9), 3.48 (brd, 1 H, J = 5.6 Hz, H-14), 3.51 (s, 3 H, OCH₃), 4.09 (brd, 1 H, J = 5.6 Hz, NH), 5.59 (d, J = 6.0 Hz, 1 H, H-7), 6.85 (dd, J = 8.2, 1.9 Hz, 1 H, H-6'), 7.21 (t, J = 8.2 Hz, 1 H, H-5'), 7.42 (t, J = 1.9 Hz, 1 H, H-2'), 7.44 (dd, J = 8.2, 1.9 Hz, 1 H, H-4'); ¹³C NMR (151 MHz, CDCl₃): see Table S2. IR (neat): ν = 671, 735, 758, 826, 1103, 1121, 1146, 1190, 1215, 1250, 1348, 1385, 1433, 1460, 1477, 1528, 1582, 1622, 1713, 2855, 2870, 2878, 2930, 2949, 3408 cm⁻¹. UV (EtOH) λ_{max} nm (lg ϵ): 250 (4.5), 408 (3.2). MS (EI): m/z (%) = 454 (4), 440 (1), 437 (6), 318 (5), 317 (21), 287 (6), 285 (4), 258 (19), 257 (100), 256 (4), 201 (8), 199 (5), 173 (6), 161 (4), 145 (5), 121 (13), 119 (6), 105 (6), 93 (5), 91 (5), 85 (9), 83 (16), 55 (7), 47 (5), 41 (4); calcd. for C₂₇H₃₈O₄N₂: 454.2826, found 454.2818.

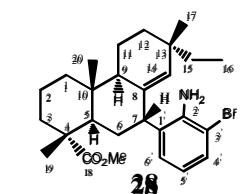
(1*R*,4*aR*,4*bR*,7*S*,9*R*,10*aR*)-Methyl 7-ethyl-9-hydroxy-1,4*a*,7-trimethyl-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (14). mp 60-62°C. $[\alpha]_D$ = +94.4 (c 1.1, CHCl₃). HRMS calcd. for C₂₁H₃₄O₃: 334.2502, found 334.2496. The ¹H NMR and ¹³C NMR spectra agreed with those published⁹.

(1*R*,4*aR*,4*bR*,7*S*,9*R*,10*aR*)-Methyl 9-((2-bromophenyl)amino)-7-ethyl-1,4*a*,7-trimethyl-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (22).



R_f = 0.66 (CHCl₃); $[\alpha]_D$ = +1.96 (c 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.73 (t, J = 7.5 Hz, 3 H, CH₃-16), 0.86 (s, 3 H, CH₃-20), 0.90 (s, 3 H, CH₃-17), 1.17 (m, 2 H, H-1,12), 1.21 (s, 3 H, CH₃-19), 1.20 (m, 2 H, CH₂-15), 1.29 (m, 1 H, H-12), 1.42 (m, 1 H, H-6), 1.50, 1.53, 1.58, 1.60 (all m, 5 H, CH₂-2,11, H-3), 1.73 (ddd, J = 13.6, 12.4, 3.8 Hz, 1 H, H-6), 1.78 (m, 2 H, H-3,1), 2.08 (m, 1 H, H-9), 2.34 (dd, J = 12.4, 2.0 Hz, 1 H, H-5), 3.42 (s, 3 H, OCH₃), 3.95 (dd, J = 3.8, 1.5 Hz, 1 H, H-7), 4.05 (brs, 1 H, NH), 5.53 (s, 1 H, H-14), 6.48 (dt, J = 7.5, 1.8 Hz, 1 H, H-4'), 6.67 (dd, J = 7.5, 1.8 Hz, 1 H, H-6'), 7.09 (dt, J = 7.5, 1.6 Hz, 1 H, H-5'), 7.38 (dd, J = 7.5, 1.6 Hz, 1 H, H-3'); ¹³C NMR (101 MHz, CDCl₃): see Table S2. IR (neat): ν = 740, 1018, 1064, 1120, 1145, 1157, 1190, 1244, 1282, 1315, 1384, 1431, 1446, 1460, 1508, 1595, 1616, 1726, 2850, 2868, 2947, 3381 cm⁻¹. UV (EtOH) λ_{max} nm (lg ϵ): 241 (4.05), 475 (3.46). MS (EI): m/z (%) = 487 (24), 287 (42), 257 (91), 173 (97), 171 (100), 121 (22), 92 (38), 65 (43), 47 (33), 35 (14); calcd. for C₂₇H₃₈O₂NBr: 487.2080, found 487.2076.

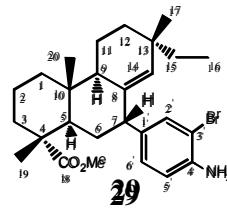
(1*R*,4*aR*,4*bR*,7*S*,9*R*,10*aR*)-Methyl 9-(2-amino-3-bromophenyl)-7-ethyl-1,4*a*,7-trimethyl-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (28).



R_f = 0.68 (CHCl₃); $[\alpha]_D$ = -15.89 (c 0.2, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.71 (t, J = 7.5 Hz, 3 H, CH₃-16), 0.88 (m, 1 H, H-1), 0.89 (s, 3 H, CH₃-20), 0.93 (s, 3 H, CH₃-17), 1.16 (s, 3 H, CH₃-19), 1.21-1.26 (m, 2 H, CH₂-15), 1.38-1.56 (m, 8 H, CH₂-12,2,11, H-3,6), 1.61 (m, 2 H, H-3,1), 1.70 (m, 1 H, H-5), 1.80 (m, 1 H, H-9), 2.22 (m, 1 H, H-6), 3.15

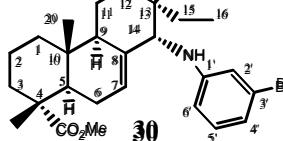
(s, 3 H, OCH₃), 3.53 (d, *J* = 4.8 Hz, 1 H, H-7), 4.08 (brs, 2 H, NH₂), 5.35 (s, 1 H, H-14), 6.57 (t, *J* = 7.8 Hz, 1 H, H-5'), 7.06 (dd, *J* = 7.8, 1.6 Hz, 1 H, H-6'), 7.24 (dd, *J* = 7.8, 1.6 Hz, 1 H, H-4'). ¹³C NMR (101 MHz, CDCl₃): see Table S3. IR (neat): ν = 754, 1150, 1169, 1192, 1261, 1450, 1462, 1585, 1612, 1720, 2849, 2868, 2936, 2963, 3410, 3493 cm⁻¹. UV (EtOH) λ_{max} nm (lg_e): 207 (4.53), 241 (3.81), 293 (3.46). MS (EI): *m/z* (%) = 487 (6), 474 (12), 472 (14), 430 (16), 429 (25), 428 (16), 427 (23), 412 (30), 414 (28), 398 (9), 358 (10), 306 (12), 287 (17), 257 (10), 242 (20), 241 (100), 227 (15), 197 (8), 196 (8), 186 (9), 184 (9), 182 (11), 121 (8), 71 (21), 59 (8), 55 (10), 41 (6); calcd. for C₂₇H₃₈O₂NBr: 487.2080, found 487.2076.

(1*R*,4*aR*,4*bR*,7*S*,9*S*,10*aR*)-Methyl 9-(4-amino-3-bromophenyl)-7-ethyl-1,4*a*,7-trimethyl-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (29).



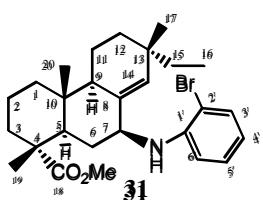
*R*_f = 0.68 (CHCl₃); [α]_D = -37.89 (*c* 0.3, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.85 (t, *J* = 7.5 Hz, 3 H, CH₃-16), 0.88 (s, 3 H, CH₃-20), 0.94 (s, 3 H, CH₃-17), 1.03 (m, 1 H, H-1), 1.20 (s, 3 H, CH₃-19), 1.32 (q, *J* = 7.5 Hz, 2 H, CH₂-15), 1.36 (m, 2 H, CH₂-12), 1.49 (m, 3 H, H-2,11,3), 1.60 (m, 3 H, H-2,11,6), 1.69 (m, 2 H, H-3,1), 1.79 (dd, *J* = 12.2, 2.4 Hz, 1 H, H-5), 1.87 (m, 2 H, H-6,9), 3.39 (d, *J* = 4.8 Hz, 1 H, H-7), 3.56 (s, 3 H, OCH₃), 5.38 (s, 1 H, H-14), 6.65 (d, *J* = 8.6 Hz, 1 H, H-5'), 6.95 (d, *J* = 8.6 Hz, 1 H, H-6'), 7.29 (s, 1 H, H-2'). ¹³C NMR (101 MHz, CDCl₃): see Table S3. IR (neat): ν = 756, 816, 1142, 1163, 1173, 1190, 1250, 1308, 1385, 1435, 1460, 1503, 1620, 1722, 2851, 2870, 2945, 3373 cm⁻¹. UV (EtOH) λ_{max} nm (lg_e): 206 (3.23), 242 (3.93), 298 (4.43). MS (EI): *m/z* (%) = 487 (3), 460 (37), 458 (36), 321 (42), 319 (43), 287 (55), 241 (33), 227 (52), 225 (40), 197 (40), 186 (100), 184 (100), 182 (31), 181 (31), 159 (33), 157 (37), 146 (45), 145 (36), 121 (45), 105 (30), 95 (46), 81 (33), 55 (30), 41 (30); calcd. for C₂₇H₃₈O₂NBr: 487.2080, found 487.2084

(1*R*,4*aR*,4*bR*,7*S*,8*S*,10*aR*)-Methyl 8-((2-bromophenyl)amino)-7-ethyl-1,4*a*,7-trimethyl-1,2,3,4,4*a*,4*b*,5,6,7,8,10,10*a*-dodecahydrophenanthrene-1-carboxylate (30).



*R*_f = 0.68 (CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.76 (t, *J* = 7.5 Hz, 3 H, CH₃-16), 0.85 (s, 3 H, CH₃-17), 0.87 (s, 3 H, CH₃-20), 1.10 (m, 1 H, H-1), 1.22 (s, 3 H, CH₃-19), 1.22-1.35 (m, 2 H, H-15), 1.39-1.43 (m, 4 H, CH₂-12, H-11,2), 1.47-1.61 (m, 6 H, CH₂-6,3, H-2,11), 1.68 (dd, *J* = 12.1, 3.0 Hz, 1 H, H-5), 1.81 (m, *J*_{gem} = 13.0 Hz, 1 H, H-1), 1.90 (m, 1 H, H-9), 3.45 (brs, 1 H, H-14), 3.54 (s, 3 H, OCH₃), 5.50 (brd, *J* = 5.9 Hz, 1 H, H-7), 6.49 (dt, *J* = 8.1, 1.6 Hz, 1 H, H-4'), 6.71 (d, *J* = 8.1, 1 H, H-6'), 7.09 (dt, *J* = 8.1, 1.6 Hz, 1 H, H-5'), 7.38 (dd, *J* = 8.1, 1.6 Hz, 1 H, H-3'). ¹³C NMR (101 MHz, CDCl₃): see Table S3. IR (neat): ν = 738, 1016, 1062, 1105, 1120, 1145, 1188, 1244, 1280, 1321, 1384, 1431, 1462, 1510, 1595, 1695, 1726, 2850, 2868, 2925, 3417 cm⁻¹. UV (EtOH) λ_{max} nm (lg_e): 249 (3.76), 301 (3.10). MS (EI): *m/z* (%) = 487 (21), 317 (57), 287 (21), 257 (100), 207 (19), 201 (19), 173 (10), 147 (12), 133 (10), 105 (12), 41 (5); calcd. for C₂₇H₃₈O₂NBr: 487.2080, found 487.2068.

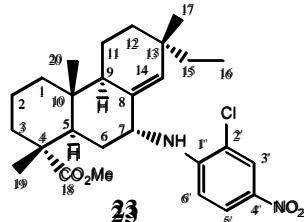
(1*R*,4*aR*,4*bR*,7*S*,9*S*,10*aR*)-Methyl 9-((2-bromophenyl)amino)-7-ethyl-1,4*a*,7-trimethyl-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (31).



*R*_f = 0.68 (CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.79 (s, 3 H, CH₃-20), 0.82 (t, *J* = 7.5 Hz, 3 H, CH₃-16), 0.89 (s, 3 H, CH₃-17), 1.17 (s, 3 H, CH₃-19), 1.20 (m, 1 H, H-1), 1.24-1.29 (m, 3 H, CH₂-15, H-12), 1.34 (m, 1 H, H-12), 1.41-1.83 (m, 9 H, CH₂-6,2,11,3, H-1), 2.01 (m, 1 H, H-9), 2.35 (dd, *J* = 12.2, 2.8 Hz, 1 H, H-5), 3.55 (ddd, *J* = 12.2, 4.9, 3.0 Hz, 1 H, H-7), 3.65 (s, 3 H, OCH₃), 4.07 (brd, *J* = 4.9 Hz, 1 H, NH), 5.36 (s, 1 H, H-14), 6.61 (dt, *J* = 8.4, 1.8 Hz, 1 H, H-4'), 6.76 (dd, *J* = 8.4, 1.8 Hz, 1 H, H-6'), 7.09 (dt, *J* = 8.4, 1.5 Hz, 1 H, H-5'), 7.39 (dd, *J* = 8.4, 1.5 Hz, 1 H, H-3'). ¹³C NMR (101 MHz, CDCl₃): see Table S3. IR (neat): ν = 756, 816, 1142, 1163, 1173, 1190,

1250, 1308, 1385, 1435, 1460, 1503, 1620, 1722, 2851, 2870, 2945, 3373 cm⁻¹. UV (EtOH) λ_{max} nm (lg ϵ): 206 (3.23), 242 (3.93), 298 (4.43). MS (EI): *m/z* (%) = 487 (23), 362 (40), 317 (26), 287 (63), 257 (76), 241 (31), 227 (43), 194 (100), 166 (75), 161 (57), 145 (23), 121 (41), 109 (26), 107 (26), 105 (29), 95 (36), 93 (29), 91 (23), 81 (30), 55 (31), 41 (23); calcd. for C₂₇H₃₈O₂NBr: 487.2080, found 487.2083.

(1*R*,4*aR*,4*bR*,7*S*,9*R*,10*aR*)-Methyl carboxylate (23).



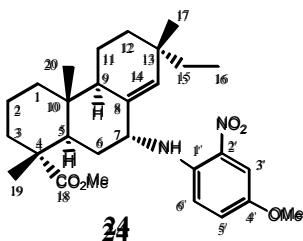
calcd. for C₂₇H₃₇O₄N₂Cl: 488.2436, found 488.2433.

9-((2-chloro-4-nitrophenyl)amino)-7-ethyl-1,4a,7-trimethyl-1,2,3,4,4a,4b,5,6,7,9,10,10a-dodecahydronaphthalene-1-carboxylate (23).

*R*_f = 0.66 (CHCl₃); [α]_D = + 95.33 (c 0.3, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.77 (t, *J* = 7.5 Hz, 3 H, CH₃-16), 0.87 (s, 3 H, CH₃-20), 0.92 (s, 3 H, CH₃-17), 1.15, 1.18 (both m, 2 H, H-1,12), 1.22 (s, 3 H, CH₃-19), 1.23 (m, 2 H, H-15), 1.30 (m, 1 H, H-12), 1.43 (dd, *J* = 12.4, 2.2 Hz, 1 H, H-6), 1.57-1.62 (m, 5 H, CH₂-2,11, H-3), 1.66 (m, 1 H, H-3), 1.74 (m, *J*_{gem} = 12.9 Hz, 1 H, H-1), 1.86 (ddd, *J* = 13.6, 12.4, 2.6 Hz, 1 H, H-6), 2.00 (dd, *J* = 8.5, 1.8 Hz, 1 H, H-9), 2.31 (dd, *J* = 12.4, 2.2 Hz, 1 H, H-5), 3.52 (s, 3 H, OCH₃), 4.04 (dd, *J* = 5.2, 2.6 Hz, 1 H, H-7), 5.58 (d, *J* = 5.2 Hz, 1 H, NH), 5.63 (s, 1 H, H-14), 6.70 (d, *J* = 9.1 Hz, 1 H, H-6'), 8.00 (dd, *J* = 9.1, 2.7 Hz, 1 H, H-5'), 8.19 (d, *J* = 2.7 Hz, 1 H, H-3'). ¹³C NMR (101 MHz, CDCl₃): see Table S2. IR (neat): ν = 746, 894, 1062, 1122, 1139, 1245, 1282, 1325, 1448, 1458, 1500, 1527, 1589, 1720, 2852, 2868, 2949, 3402 cm⁻¹. UV (EtOH) λ_{max} nm (lg ϵ): 373 (4.84). MS (EI): *m/z* (%) = 488 (5), 318 (11), 317 (45), 258 (22), 257 (100), 121 (26), 105 (11), 81 (8), 55 (11), 41 (8);

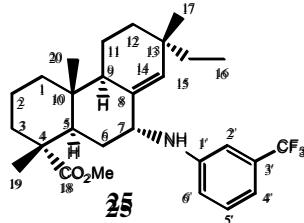
calcd. for C₂₇H₃₇O₄N₂Cl: 488.2436, found 488.2433.

(1*R*,4*aR*,4*bR*,7*S*,9*R*,10*aR*)-Methyl 7-ethyl-9-((4-methoxy-2-nitrophenyl)-amino)-1,4a,7-trimethyl-1,2,3,4,4a,4b,5,6,7,9,10,10a-dodecahydronaphthalene-1-carboxylate (24).



M.p. 174-176°C (MeOH); *R*_f = 0.63 (CHCl₃); [α]_D = - 213.33 (c 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.73 (t, *J* = 7.5 Hz, 3 H, CH₃-16), 0.86 (s, 3 H, CH₃-20), 0.91 (s, 3 H, CH₃-17), 1.12-1.19 (m, 2 H, H-1,12), 1.20 (s, 3 H, CH₃-19), 1.23 (m, 2 H, CH₂-15), 1.30 (m, 1 H, H-12), 1.43 (m, *J*_{gem} = 13.4 Hz, 1 H, H-6), 1.47-1.62 (m, 5 H, CH₂-2,11, H-3), 1.72 (m, 1 H, H-3), 1.75 (m, 1 H, H-1), 1.81 (ddd, *J* = 13.4, 12.2, 3.0 Hz, 1 H, H-6), 2.06 (dd, *J* = 8.5, 1.6 Hz, 1 H, H^a-9), 2.34 (dd, *J* = 12.2, 2.2 Hz, 1 H, H-5), 3.43 (s, 3 H, OCH₃), 3.77 (s, 3 H, C-4'-OCH₃), 4.14 (dd, *J* = 6.0, 3.0 Hz, 1 H, H-7), 5.57 (s, 1 H, H-14), 6.89 (d, *J* = 9.1 Hz, 1 H, H-6'), 7.07 (dd, *J* = 9.1, 2.6 Hz, 1 H, H-5'), 7.58 (d, *J* = 2.6 Hz, 1 H, H-3'), 8.48 (d, *J* = 6.0 Hz, 1 H, NH). ¹³C NMR (101 MHz, CDCl₃): see Table S2. IR (neat): ν = 759, 931, 1041, 1049, 1062, 1141, 1190, 1240, 1284, 1344, 1411, 1444, 1460, 1517, 1571, 1726, 2850, 2868, 2949, 3352 cm⁻¹. UV (EtOH) λ_{max} nm (lg ϵ): 241 (4.05), 475 (3.46). MS (EI): *m/z* (%) = 484 (28), 317 (24), 287 (36), 258 (21), 257 (100), 227 (11), 168 (18), 121 (24), 41 (3); calcd. for C₂₇H₄₀O₅N₂: 484.2932, found 484.2930.

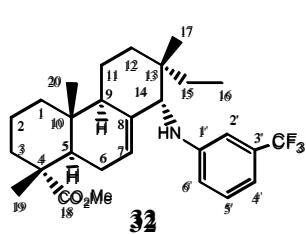
(1*R*,4*aR*,4*bR*,7*S*,9*R*,10*aR*)-Methyl 7-ethyl-1,4a,7-trimethyl-9-((3-(trifluoromethyl)phenyl)amino)-1,2,3,4,4a,4b,5,6,7,9,10,10a-dodecahydro-phenanthrene-1-carboxylate (25).



*R*_f = 0.49 (CHCl₃); [α]_D = + 3.2 (c 0.2, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.74 (t, *J* = 7.5 Hz, 3 H, CH₃-16), 0.86 (s, 3 H, CH₃-20), 0.90 (s, 3 H, CH₃-17), 1.15 (m, 2 H, H-1,12), 1.21 (s, 3 H, CH₃-19), 1.31 (m, 2 H, CH₂-15), 1.41 (m, 1 H, H-12), 1.44 (m, 1 H, H-6), 1.55 (m, 2 H, CH₂-2), 1.60-1.64 (m, 3 H, CH₂-11, H-3), 1.73 (m, 2 H, H-1,3), 1.76 (m, 1 H, H-6), 2.05 (dd, *J* = 8.7, 1.8 Hz, 1 H, H-9), 2.28 (dd, *J* = 12.2, 2.2 Hz, 1 H, H-5), 3.39 (s, 3 H, OCH₃), 3.91 (brd, 1 H, H-7), 4.17 (brs, 1 H, NH), 5.57 (s, 1 H, H-14), 6.73 (d, *J* = 7.5 Hz, 1 H, H-6'), 6.83 (s, 1 H, H-2'), 6.84 (d, *J* = 7.5 Hz, 1 H, H-4'), 7.19 (t, *J* = 7.5 Hz, 1 H, H-5'). ¹³C NMR (101 MHz, CDCl₃): see Table S2. IR (neat): ν = 698, 758, 781, 860, 871, 993, 1066, 1122, 1163, 1244, 1346, 1438, 1479, 1492, 1614, 1716, 2852, 2870, 2949, 3404 cm⁻¹. UV (EtOH) λ_{max} nm (lg ϵ): 259 (3.95), 312

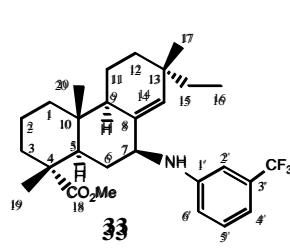
(3.13). MS (EI): m/z (%) = 477 (22), 454 (11), 317 (28), 258 (18), 257 (100), 256 (4), 227 (7), 161 (6), 121 (18), 105 (8), 55 (8), 41 (6); calcd. for $C_{28}H_{38}O_2NF_3$: 477.2849, found 477.2842.

(1*R*,4*aR*,4*bR*,7*S*,8*S*,10*aR*)-Methyl 7-ethyl-1,4a,7-trimethyl-8-((3-(trifluoromethyl)phenyl)-amino)-1,2,3,4,4*a*,4*b*,5,6,7,8,10,10*a*-dodecahydrophenanthrene-1-carboxylate (32).



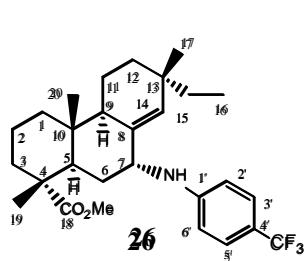
R_f = 0.49 (CH₃Cl); ¹H NMR (400 MHz, CDCl₃): δ = 0.78 (t, J = 7.5 Hz, 3 H, CH₃-16), 0.85 (s, 3 H, CH₃-17), 0.87 (s, 3 H, CH₃-20), 1.06 (m, 1 H, H-1), 1.21 (s, 3 H, CH₃-19), 1.32-1.36 (m, 2 H, H-15), 1.41 (m, 4 H, CH₂-12, H-11,2), 1.47-1.55 (m, 6 H, CH₂-6,3, H-2,11), 1.64 (dd, J = 11.8, 2.8 Hz, 1H, H-5), 1.81 (m, J_{gem} = 13.2 Hz, 1 H, H-1), 1.88 (m, 1 H, H-9), 3.43 (brs, 1 H, H^b-14), 3.51 (s, 3 H, OCH₃), 3.91 (brs, 1 H, NH), 5.52 (d, J = 5.4 Hz, 1 H, H-7), 6.73 (d, J = 8.1 Hz, 1 H, H-6'), 6.80 (s, 1 H, H-2'), 6.85 (d, J = 8.1 Hz, 1 H, H-4'), 7.19 (t, J = 8.1 Hz, 1 H, H-5'). ¹³C NMR (101 MHz, CDCl₃): see Table S3. IR (neat): ν = 698, 758, 783, 993, 1066, 1122, 1163, 1247, 1280, 1319, 1344, 1384, 1435, 1444, 1460, 1481, 1492, 1519, 1614, 1714, 1724, 2854, 2871, 2929, 3404 cm⁻¹. UV (EtOH) λ_{max} nm (lg ϵ): 257 (4.18), 312 (3.38). MS (EI): m/z (%) = 477 (8), 317 (58), 287 (20), 257 (100), 227 (10), 173 (12), 161 (9), 145 (12), 121 (23), 105 (10), 93 (9), 41 (5); calcd. for $C_{28}H_{38}O_2NF_3$: 477.2849, found 477.2842.

(1*R*,4*aR*,4*bR*,7*S*,9*S*,10*aR*)-Methyl 7-ethyl-1,4a,7-trimethyl-9-((3-(trifluoromethyl)phenyl)-amino)-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (33).



R_f = 0.49 (CHCl₃); $[\alpha]_D$ = -34.1 (c 0.2, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.64 (t, J = 7.5 Hz, 3 H, CH₃-16), 0.84 (s, 3 H, CH₃-20), 0.86 (s, 3 H, CH₃-17), 1.11-1.17 (m, 3 H, CH₂-15, H-1), 1.20 (s, 3 H, CH₃-19), 1.24-1.32 (m, 2 H, CH₂-12), 1.39 (m, J_{gem} = 13.0 Hz, 1 H, H-6), 1.49-1.59 (m, 4 H, CH₂-2, H-11,6), 1.62 (m, 1 H, H-3), 1.67 (m, 1 H, H-11), 1.70-1.78 (m, 2 H, H-1,3), 1.90 (dd, J = 8.4, 1.8 Hz, 1 H, H-9), 2.07 (dd, J = 12.4, 2.7 Hz, 1 H, H-5), 3.64 (s, 3 H, OCH₃), 3.70 (ddd, J = 12.0, 4.8, 2.8 Hz, 1 H, H-7), 3.89 (m, 1 H, NH), 5.38 (s, 1 H, H-14), 6.66 (d, J = 8.1 Hz, 1 H, H-6'), 6.69 (s, 1 H, H-2'), 6.85 (d, J = 8.1 Hz, 1 H, H-4'), 7.19 (t, J = 8.1 Hz, 1 H, H-5'). ¹³C NMR (101 MHz, CDCl₃): see Table S3 (Supp. Info). IR (neat): ν = 698, 756, 783, 858, 871, 993, 1068, 1122, 1163, 1244, 1344, 1444, 1517, 1614, 1718, 2852, 2870, 2933, 3398 cm⁻¹. UV (EtOH) λ_{max} nm (lg ϵ): 256 (3.92), 312 (3.13). MS (EI): m/z (%) = 477 (38) [M]⁺, 475 (11), 317 (28), 287 (20), 258 (20), 257 (100), 255 (10), 173 (14), 161 (15), 121 (32), 105 (20), 55 (19), 41 (15); calcd. for $C_{28}H_{38}O_2NF_3$: 477.2849, found 477.2843.

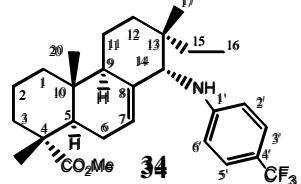
(1*R*,4*aR*,4*bR*,7*S*,9*R*,10*aR*)-Methyl 7-ethyl-1,4a,7-trimethyl-9-((4-(trifluoromethyl)phenyl)-amino)-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (26).



R_f = 0.63 (CHCl₃); $[\alpha]_D$ = +22.98 (c 0.7, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.75 (t, J = 7.5 Hz, 3 H, CH₃-16), 0.85 (s, 3 H, CH₃-20), 0.91 (s, 3 H, CH₃-17), 1.15 (m, 2 H, H-1,12), 1.20 (s, 3 H, CH₃-19), 1.30 (m, 2 H, CH₂-15), 1.40 (m, 1 H, H-12), 1.43 (m, 1 H, H-6), 1.50-1.63 (m, 6 H, CH₂-2,11,3), 1.71 (m, 1 H, H-1), 1.73 (m, 1 H, H-6), 2.02 (dd, J = 8.6, 1.8 Hz, 1 H, H-9), 2.24 (dd, J = 12.0, 1.8 Hz, 1 H, H-5), 3.37 (s, 3 H, OCH₃), 3.62 (d, 1 H, J = 5.2, NH), 3.92 (brd, 1 H, J = 5.2, H-7), 5.56 (s, 1 H, H-14), 6.60 (d, J = 8.5 Hz, 2 H, H-2',6'), 7.33 (d, J = 8.5 Hz, 2 H, H-3',5'). ¹³C NMR (101 MHz, CDCl₃): see Table S2. IR (neat): ν = 758, 823, 1060, 1082, 1110, 1159, 1186, 1242, 1251, 1325, 1365, 1435, 1446, 1460, 1531, 1616, 1716, 2852, 2870, 2947, 3400 cm⁻¹. UV (EtOH) λ_{max} nm (lg ϵ): 264 (3.97), 394 (3.06). MS (EI): m/z (%)

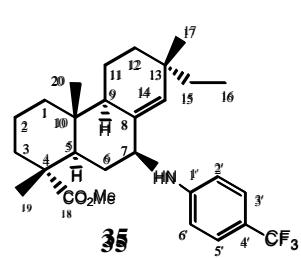
(%) = 477 (7), 317 (28), 258 (20), 257 (100), 161 (23), 145 (19), 123 (18), 121 (46), 107 (28), 93 (29), 91 (32), 81 (15), 59 (19), 55 (54), 57 (35), 43 (47), 41 (54), 39 (17); calcd. for $C_{28}H_{38}O_2NF_3$: 477.2849, found 477.2845.

(1*R*,4*aR*,4*bR*,7*S*,8*S*,10*aR*)-Methyl 7-ethyl-1,4*a*,7-trimethyl-8-((4-(trifluoromethyl)phenyl)-amino)-1,2,3,4,4*a*,4*b*,5,6,7,8,10,10*a*-dodeca-hydrophenanthrene-1-carboxylate (34).



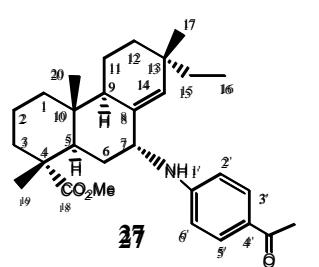
R_f = 0.63 (CHCl₃). ¹H and ¹³C NMR data of compound 34 was obtained from the spectra of a mixture of compounds 26, 34, 35 (in a ratio 2.8:1.4:1). ¹H NMR (400 MHz, CDCl₃): δ = 0.76 (t, J = 7.5 Hz, 3 H, CH₃-16), 0.85 (s, 3 H, CH₃-17), 0.88 (s, 3 H, CH₃-20), 1.07 (m, 1 H, H-1), 1.22 (s, 3 H, CH₃-19), 1.21 (m, 2 H, CH₂-15), 1.39-1.76 (m, 11 H, CH₂-12,6,3,11,2, H-5), 1.80 (m, 1 H, H-1), 1.92 (m, 1 H, H^a-9), 3.53 (s, 3 H, OCH₃), 3.49 (brd, 1 H, J = 5.8 Hz, H-14), 3.77 (d, 1 H, 3.56 (brd, 1 H, J = 5.8 Hz, NH), 5.55 (d, J = 5.9 Hz, 1 H, H-7), 6.60 (d, J = 8.5 Hz, 2 H, H-2',6'), 7.34 (d, J = 8.5 Hz, 2 H, H-3',5'). ¹³C NMR (101 MHz, CDCl₃): see Table S3.

(1*R*,4*aR*,4*bR*,7*S*,9*S*,10*aR*)-Methyl 7-ethyl-1,4*a*,7-trimethyl-9-((4-(trifluoro-methyl)phenyl)-amino)-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydro-phenanthrene-1-carboxylate (35).



R_f = 0.63 (CHCl₃); $[\alpha]_D$ = -61.67 (c 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.65 (t, J = 7.5 Hz, 3 H, CH₃-16), 0.83 (s, 3 H, CH₃-20), 0.86 (s, 3 H, CH₃-17), 1.16 (m, 2 H, H-1,12), 1.20 (s, 3 H, CH₃-19), 1.24 (m, 2 H, CH₂-15), 1.34-1.40 (m, 1 H, H-12), 1.56-1.60 (m, 5 H, CH₂-2,11, H-6), 1.62-1.81 (m, 4 H, CH₂-3, H-6,1), 1.88 (dd, J = 9.0, 2.1 Hz, 1 H, H-9), 2.05 (dd, J = 12.4, 2.1 Hz, 1 H, H-5), 3.64 (s, 3 H, OCH₃), 3.72 (ddd, J = 12.0, 6.0, 2.8 Hz, 1 H, H-7), 3.95 (m, 1 H, NH), 5.36 (s, 1 H, H-14), 6.51 (d, J = 8.6 Hz, 2 H, H-2',6'), 7.33 (d, J = 8.6 Hz, 2 H, H-3',5'). ¹³C NMR (101 MHz, CDCl₃): see Table S3. IR (neat): ν = 642, 657, 829, 1064, 1106, 1159, 1186, 1241, 1261, 1321, 1365, 1434, 1450, 1461, 1535, 1616, 1712, 2850, 2929, 2946, 3398, 3415 cm⁻¹. UV (EtOH) λ_{max} nm (lg ϵ): 221 (3.48), 322 (3.93), 350 (3.10). MS (EI): *m/z* (%) = 477 (40), 317 (25), 309 (17), 257 (100), 174 (15), 121 (30), 93 (18), 91 (18), 85 (25), 83 (44), 56 (21), 55 (32), 43 (17), 41 (27), 29 (13); calcd. for $C_{28}H_{38}O_2NF_3$: 477.2849, found 477.2853.

(1*R*,4*aR*,4*bR*,7*S*,9*R*,10*aR*)-Methyl 9-((4-acetylphenyl)amino)-7-ethyl-1,4*a*,7-trimethyl-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (27).



R_f = 0.43 (CHCl₃); $[\alpha]_D$ = +34.81 (c 1.6, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.75 (t, J = 7.5 Hz, 3 H, CH₃-16), 0.83 (s, 3 H, CH₃-20), 0.89 (s, 3 H, CH₃-17), 1.17 (s, 5 H, CH₃-19, H-1,12), 1.23 (m, 2 H, CH₂-15), 1.28 (m, 1 H, H-12), 1.43 (m, 1 H, H-6), 1.49, 1.52, 1.53, 1.60 (all m, 5 H, CH₂-2,11, H-3), 1.65, 1.70, 1.73 (all m, 3 H, H-3,1,6), 2.02 (m, 1 H, H-9), 2.24 (d, J = 12.4 Hz, 1 H, H-5), 2.45 (s, 3 H, C(O)CH₃), 3.34 (s, 3 H, OCH₃), 3.95 (brd, J = 5.4 Hz, 1 H, H-7), 4.55 (d, J = 5.4 Hz, 1 H, NH), 5.57 (s, 1 H, H-14), 6.55 (d, J = 8.3 Hz, 2 H, H-2',6'), 7.75 (d, J = 8.3 Hz, 2 H, H-3',5'). ¹³C NMR (101 MHz, CDCl₃): see Table S2. IR (neat): ν = 756, 825, 954, 1064, 1078, 1124, 1147, 1180, 1278, 1307, 1357, 1384, 1433, 1446, 1460, 1485, 1525, 1573, 1597, 1597, 1658, 1724, 2852, 2868, 2945, 3373 cm⁻¹. UV (EtOH) λ_{max} nm (lg ϵ): 238 (3.80), 335 (4.38). MS

(EI): m/z (%) = 451 (5), 287 (28), 266 (23), 257 (29), 245 (11), 241 (12), 227 (28), 166 (39), 159 (10), 151 (11), 145 (19), 135 (11), 119 (36), 109 (18), 105 (14), 95 (17), 93 (12), 91 (24), 85 (70), 82 (100), 47 (17), 28 (8). HRMS calcd. for $C_{29}H_{41}O_3N$: 451.3081, found 451.3085.

(1*R*,4*aR*,4*bR*,7*S*,8*S*,10*aR*)-Methyl 8-((4-acetylphenyl)amino)-7-ethyl-1,4*a*,7-trimethyl-1,2,3,4,4*a*,4*b*,5,6,7,8,10,10*a*-dodecahydrophenanthrene-1-carboxylate (36). Crystallized from MeOH, m.p. 163-165°C; R_f = 0.43 (CHCl₃); $[\alpha]_D$ = -196.39 (c 1.6, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.73 (t, J = 7.5 Hz, 3 H, CH₃-16), 0.84 (s, 3 H, CH₃-17), 0.87 (s, 3 H, CH₃-20), 1.07 (m, 1 H, H-1), 1.22 (s, 3 H, CH₃-19), 1.21-1.28 (m, 2 H, H-15), 1.36-1.45 (m, 4 H, CH₂-12, H-11,2), 1.50-1.61 (m, 6 H, CH₂-6,3, H-2,11), 1.72 (dd, J = 11.8, 2.6 Hz, 1 H, H-5), 1.80 (m, J_{gem} = 13.4 Hz, 1 H, H-1), 1.92 (m, 1 H, H-9), 2.48 (s, 3 H, C(O)CH₃), 3.53 (s, 3 H, OCH₃), 3.56 (brd, 1 H, J = 5.6 Hz, H-14), 3.67 (d, 1 H, J = 5.6 Hz, NH), 5.58 (d, J = 5.4 Hz, 1 H, H-7), 6.55 (d, J = 8.7 Hz, 2 H, H-2',6'), 7.77 (d, J = 8.7 Hz, 2 H, H-3',5'). ¹³C NMR (101 MHz, CDCl₃): see Table S4. IR (neat): ν = 592, 829, 1076, 1103, 1122, 1145, 1180, 1245, 1280, 1309, 1359, 1384, 1433, 1460, 1529, 1573, 1595, 1651, 1724, 2870, 2929, 3384 cm⁻¹. UV (EtOH) λ_{max} nm (lg_e): 238 (3.7), 337 (4.4). MS (EI): m/z (%) = 451 (38), 317 (32), 287 (33), 258 (21), 257 (100), 227 (20), 161 (80), 145 (15), 136 (14), 135 (11), 121 (25), 120 (21), 105 (15), 95 (11), 91 (14), 81 (11), 55 (14), 41 (11); calcd. for $C_{29}H_{41}O_3N$: 451.3081, found 451.3079.

(1*R*,4*aR*,4*bR*,7*S*,9*S*,10*aR*)-Methyl 7-ethyl-1,4*a*,7-trimethyl-9-(methyl(4-nitrophenyl)-amino)-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (38).

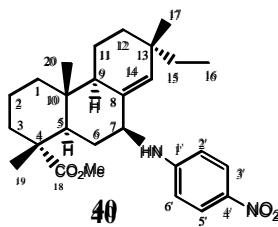
R_f = 0.66 (CHCl₃); $[\alpha]_D$ = -157.78 (c 0.3, CHCl₃); ¹H NMR (600 MHz, CDCl₃): δ = 0.61 (t, J = 7.5 Hz, 3 H, CH₃-16), 0.87 (s, 3 H, CH₃-20), 1.10 (q, J = 7.5 Hz, 2 H, CH₂-15), 1.13 (m, 1 H, H-1), 1.24 (s, 6 H, CH₃-19,17), 1.32 (m, 3 H, CH₂-12, H-6), 1.50-1.63 (m, 4 H, CH₂-2, H-3,11), 1.69 (m, 2 H, H-11,3), 1.72-1.83 (m, 2 H, H-1,6), 1.89 (dd, J = 7.9, 1.8 Hz, 1 H, H-9), 2.04 (dd, J = 12.8, 1.8 Hz, 1 H, H-5), 2.93 (s, 3 H, CH₃-N), 3.61 (s, 3 H, OCH₃), 4.24 (dd, J = 11.9, 3.0 Hz, 1 H, H-7), 4.95 (brs, 1 H, H-14), 6.57 (d, J = 8.8 Hz, 2 H, H-2',6'), 8.07 (d, J = 8.8 Hz, 2 H, H-3',5'). ¹³C NMR (151 MHz, CDCl₃): see Table S4. IR (neat): ν = 754, 786, 827, 1109, 1149, 1197, 1211, 1244, 1317, 1386, 1460, 1492, 1512, 1595, 1683, 1726, 2852, 2871, 2929 cm⁻¹. UV (EtOH) λ_{max} nm (lg_e): 232 (3.6), 314 (2.9), 394 (3.9). MS (EI): m/z (%) = 468 (21), 328 (32), 317 (19), 258 (16), 257 (70), 254 (19), 253 (100), 121 (21), 187 (17), 84 (26), 82 (42), 55 (26), 43 (25), 41 (31), 34 (8); calcd. for $C_{28}H_{40}O_4N_2$: 468.2983, found 468.2978.

(1*S*,4*aS*,4*bS*,7*R*,9*S*,10*aS*)-Methyl 7-ethyl-9-(((1*R*,4*aR*,4*bR*,7*S*,9*R*,10*aR*)-7-ethyl-1-(methoxy-carbonyl)-1,4*a*,7-trimethyl-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthren-9-yl)oxy)-1,4*a*,7-trimethyl-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (39).

R_f = 0.66 (CHCl₃); $[\alpha]_D$ = +60 (c 0.3, CHCl₃); ¹H NMR (600 MHz, CDCl₃): δ = 0.76 (s, 6 H, 2CH₃-20), 0.83 (t, J = 7.5 Hz, 6 H, 2CH₃-16), 0.88 (s, 6 H, 2CH₃-17), 1.05 (m, 4 H, 2H-1,6), 1.18 (s, 6 H, 2CH₃-19), 1.20 (m, 2 H, 2H-15), 1.23-1.27 (m, 6 H, 2CH₂-12, 2H-3), 1.30 (m, 2 H, 2H-15), 1.39 (m, 2 H, 2H-11), 1.53 (m, 8 H, 2CH₂-2, 2H-11,6), 1.57 (m, 2 H, 2H-3), 1.68 (m, 2 H, 2H-1), 1.96 (m, 2 H, 2H-9), 2.40 (dd, J = 12.4, 2.5 Hz, 2 H, 2H-5), 3.51 (dd, J = 4.6, 2.4 Hz, 2 H, 2H-7), 3.80 (s, 6 H, 2OCH₃), 5.17 (brs, 2 H, 2H-14). ¹³C NMR (151 MHz, CDCl₃): see Table S4. IR (neat): ν = 1037, 1060, 1082, 1122, 1143, 1186, 1245, 1384, 1433, 1460, 1597, 1728, 2850, 2871.

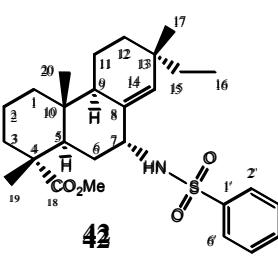
2925, 2945, 3435 cm^{-1} . UV (EtOH) λ_{\max} nm (lg ϵ): 243 (3.6), 306 (2.7). MS (EI): m/z (%) = 650 (3), 334 (72), 317 (75), 287 (42), 257 (100), 227 (13), 166 (47), 145 (10), 121 (37), 109 (17), 95 (17), 81 (15), 41 (9). HRMS calcd. for $\text{C}_{42}\text{H}_{66}\text{O}_5$: 650.4905. found 650.4899.

(1*R*,4*aR*,4*bR*,7*S*,9*S*,10*aR*)-Methyl 7-ethyl-1,4*a*,7-trimethyl-9-((4-nitrophenyl)amino)-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (40).



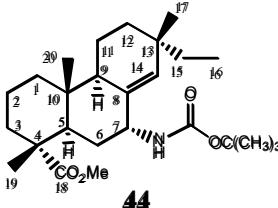
R_f = 0.66 (CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ = 0.64 (t, J = 7.7 Hz, 3 H, CH_3 -16), 0.84 (s, 3 H, CH_3 -20), 0.85 (s, 3 H, CH_3 -17), 1.14 (m, 3 H, CH_2 -15, H-1), 1.21 (s, 3 H, CH_3 -19), 1.29 (m, 2 H, CH_2 -12), 1.42 (m, 1 H, H-6), 1.49-1.77 (m, 8 H, CH_2 -11,2,3, H-6,1), 1.89 (m, 1 H, H^a -9), 2.07 (dd, J = 12.4, 2.8 Hz, 1 H, H-5), 3.65 (s, 3 H, OCH_3), 3.82 (ddd, J = 12.1, 4.8, 2.4 Hz, 1 H, H-7), 3.87 (m, 1 H, NH), 5.28 (s, 1 H, H-14), 6.45 (d, J = 8.8 Hz, 2 H, H-2',6'), 8.04 (d, J = 8.8 Hz, 2 H, H-3',5'). ^{13}C NMR (101 MHz, CDCl_3): see Table S4.

(1*R*,4*aR*,4*bR*,7*S*,9*R*,10*aR*)-Methyl 7-ethyl-1,4*a*,7-trimethyl-9-(phenyl-sulfonamido)-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (42).



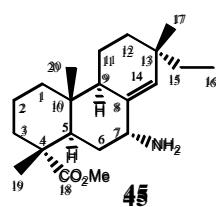
M.p.=138°C (methanol); R_f = 0.54 (CHCl_3); $[\alpha]_D$ = -3.98 (c 1.0, CHCl_3); ^1H NMR (600 MHz, CDCl_3): δ = 0.66 (t, J = 7.5 Hz, 3 H, CH_3 -16), 0.73 (s, 3 H, CH_3 -20), 0.76 (s, 3 H, CH_3 -17), 0.97 (m, 1 H, H-12), 1.00 (q, J = 7.5 Hz, 2 H, CH_2 -15), 1.09 (dt, J = 13.0, 4.3 Hz, 1 H, H-1), 1.14 (s, 3 H, CH_3 -19), 1.21 (m, 1 H, H-12), 1.34 (m, 2 H, H-6,11), 1.51 (m, 3 H, CH_2 -2, H-11), 1.61 (m, 2 H, H-6,3), 1.67 (m, 2 H, H-1,3), 1.87 (dd, J = 8.3, 1.6 Hz, 1 H, H-9), 2.20 (dd, J = 12.4, 1.8 Hz, 1 H, H-5), 3.68 (brd, J = 3.4 Hz, 1 H, H-7), 3.69 (s, 3 H, OCH_3), 4.77 (d, J = 3.4 Hz, 1 H, NH), 5.11 (s, 1 H, H-14), 7.46 (m, 2 H, H-3',5'), 7.52 (brt, J = 7.2 Hz, 1 H, H-4'), 7.82 (d, J = 7.6 Hz, 2 H, H-2',6'). ^{13}C NMR (151 MHz, CDCl_3): see Table S4. IR (neat): ν = 530, 555, 582, 646, 691, 718, 972, 1040, 1061, 1094, 1123, 1163, 1192, 1244, 1294, 1327, 1341, 1387, 1416, 1447, 1460, 1720, 2864, 2928, 2947, 3306, 3421 cm^{-1} . UV (EtOH) λ_{\max} nm (lg ϵ): 222 (3.83), 265 (2.81). MS (EI): m/z (%) = 473 (1), 445 (1), 316 (31), 301 (31), 288 (23), 287 (100), 257 (25), 237 (35), 227 (55), 166 (48), 145 (25), 123 (30), 109 (24), 107 (25), 105 (27), 95 (30), 93 (26), 91 (28), 81 (28), 79 (22), 77 (33), 67 (20), 55 (27), 41 (25); calcd. for $\text{C}_{27}\text{H}_{35}\text{O}_4\text{NS}$: 473.2594, found 473.2602.

(1*R*,4*aR*,4*bR*,7*S*,9*R*,10*aR*)-Methyl 9-((tert-butoxycarbonyl)amino)-7-ethyl-1,4*a*,7-trimethyl-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (44).



R_f = 0.49 (CHCl_3); $[\alpha]_D$ = +2.27 (c 0.4, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ = 0.77 (t, J = 7.5 Hz, 3 H, CH_3 -16), 0.79 (s, 3 H, CH_3 -20), 0.87 (s, 3 H, CH_3 -17), 1.10 (m, 2 H, H-1,12), 1.17 (s, 3 H, CH_3 -19), 1.22 (m, 1 H, H-12), 1.24 (q, J = 7.5 Hz, 2 H, CH_2 -15), 1.41 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.46-1.63 (m, 7 H, CH_2 -2,11,3, H-6), 1.66 (m, 1 H, H-6), 1.70 (m, 1 H, H-1), 1.89 (dd, J = 7.9, 1.8 Hz, 1 H, H-9), 2.02 (dd, J = 12.6, 1.8 Hz, 1 H, H-5), 3.63 (s, 3 H, OCH_3), 4.05 (brs, 1 H, H-7), 4.82 (brs, 1 H, NH), 5.53 (s, 1 H, H-14). ^{13}C NMR (101 MHz, CDCl_3): see Table S4. IR (neat): ν = 1026, 1047, 1172, 1244, 1365, 1388, 1462, 1489, 1720, 2852, 2870, 2949, 3442 cm^{-1} . UV (EtOH) λ_{\max} nm (lg ϵ): 243 (2.6). MS (EI): m/z (%) = 433 (1), 332 (16), 317 (20), 316 (35), 302 (13), 301 (41), 288 (21), 287 (100), 257 (14), 256 (12), 241 (11), 227 (13), 209 (9), 85 (20), 83 (30), 57 (17), 41 (7); calcd. for $\text{C}_{26}\text{H}_{43}\text{O}_4\text{N}$: 433.3183, found 433.3187.

(1*R*,4*aR*,4*bR*,7*S*,9*R*,10*aR*)-Methyl 9-amino-7-ethyl-1,4*a*,7-trimethyl-1,2,3,4,4*a*,4*b*,5,6,7,9,10,10*a*-dodecahydrophenanthrene-1-carboxylate (45).



$R_f = 0.43$ (CHCl_3); $[\alpha]_D = +25.59$ ($c\ 0.3, \text{CHCl}_3$). ^1H NMR (400 MHz, CDCl_3): δ = 0.76 (s, 3 H, CH_3 -20), 0.78 (t, J = 7.5 Hz, 3 H, CH_3 -16), 0.87 (s, 3 H, CH_3 -17), 1.17 (s, 3 H, CH_3 -19), 1.22 (m, 5 H, CH_2 -15,12 H-1), 1.38-1.71 (m, 7 H, CH_2 -2,11,3, H-6), 1.90-2.13 (m, 2 H, H-6,1), 2.18 (dd, J = 7.9, 1.8 Hz, 1 H, H-9), 2.29 (dd, J = 12.2, 2.4 Hz, 1 H, H-5), 3.19 (m, 2 H, NH_2), 3.66 (s, 3 H, OCH_3), 3.72 (d, J = 3.8 Hz, 1 H, H-7), 5.40 (s, 1 H, H-14). ^{13}C NMR (101 MHz, CDCl_3): see Table S4. IR (neat): ν = 1061, 1105, 1115, 1130, 1150, 1177, 1190, 1244, 1385, 1460, 1726, 2853, 2868, 2928, 2945 cm^{-1} . UV (EtOH) λ_{max} nm (lg ϵ): 231 (3.34), 256 (3.07). MS (EI): m/z (%) = 332 (5), 330 (3), 319 (1), 318 (3), 316 (12), 287 (29), 257 (14), 256 (12), 241 (18), 227 (40), 187 (12), 171 (11), 165 (45), 159 (10), 150 (23), 145 (20), 137 (15), 136 (100), 133 (13), 131 (14), 119 (13), 107 (11), 105 (16), 95 (16), 93 (13), 91 (16), 81 (11), 79 (14), 67 (7), 55 (10); calcd. for $\text{C}_{21}\text{H}_{35}\text{O}_2\text{N}$: 333.2662, found 332.2590.

Table S1. ^{13}C NMR Spectral data for compounds **4-7, 10-13** (CDCl_3 , δ , ppm).

C atom	4	5	6	7	10	11	12	13
1	38.12	36.43	37.08	38.16	38.26	38.78	38.22	37.99
2	18.11	18.06	18.23	18.04	18.00	17.84	18.03	18.06
3	36.54	35.93	36.25	36.43	37.05	36.69	37.06	36.81
4	47.14	44.30	46.93	47.31	46.77	46.28	46.85	47.17
5	43.12	50.26	44.09	43.90	42.91	44.73	42.94	47.43
6	29.25	127.20	116.44	28.56	29.73	24.89	29.77	32.49
7	55.52	130.97	121.65	45.29	56.39	125.02	56.40	56.24
8	134.13	134.80	131.79	133.71	133.95	136.32	134.20	118.42
9	47.10	50.57	145.77	48.48	47.32	47.52	47.16	49.80
10	38.07	36.43	43.32	37.99	38.09	35.00	38.13	37.87
11	18.35	18.68	25.70	18.71	18.33	19.31	18.33	18.86
12	32.67	33.13	32.42	33.14	32.75	31.21	32.96	32.83
13	34.24	35.02	31.66	34.46	34.28	36.61	34.16	33.85
14	138.10	135.75	38.31	137.42	138.58	62.44	137.83	131.26

15	35.96	35.87	36.33	36.43	35.93	32.24	35.92	35.25
16	8.08	8.30	8.04	8.34	8.14	7.40	7.96	8.01
17	25.06	26.92	25.04	25.48	24.91	20.95	24.78	25.53
18	178.52	178.77	179.03	178.85	179.00	178.84	1798.99	178.87
19	17.00	17.11	21.65	16.99	16.82	17.41	16.80	17.00
20	14.48	13.61	17.11	15.21	14.69	15.28	14.60	15.05
1'	144.26			135.08	152.44	152.77	147.97	148.68
2'	131.83			135.46	111.69	113.61	107.19	106.51
3'	126.86			132.07	126.18	126.37	149.08	149.30
4'	114.79			142.60	126.08	137.24	111.04	111.30
5'	135.58			118.16	126.18	126.37	129.23	129.42
6'	115.02			124.51	111.69	113.61	119.59	118.72
OCH ₃	51.86	51.94	51.87	51.78	51.98	51.91	51.88	52.10

Table S2. ^{13}C NMR Spectral data for compounds **15**, **22-27** (CDCl_3 , δ , ppm).

C atom	15	22	23	24	25	26	27	
1	38.90	38.29	38.26	38.23	38.29	38.31	38.25	
2	17.89	18.16	18.04	18.15	18.38	18.10	18.02	
3	36.67	36.70	36.95	36.64	36.93	36.90	36.86	
4	46.32	47.20	46.93	47.19	47.00	47.01	46.91	
5	44.84	43.14	43.11	43.16	42.99	42.98	42.91	
6	24.9	29.37	30.12	29.71	29.41	29.27	29.37	
7	124.77	56.17	56.36	55.83	56.30	56.20	56.01	
8	135.21	134.69	133.51	135.61	134.78	134.80	134.53	
9	47.61	47.14	47.08	47.00	47.27	47.36	47.32	
10	34.97	38.10	38.18	38.11	37.29	38.07	37.99	
11	19.47	18.40	18.32	18.39	18.38	18.38	18.32	
12	31.54	32.92	32.65	32.71	33.04	32.90	32.83	
13	36.50	34.13	34.36	34.27	33.10	34.16	34.13	
14	62.95	137.26	138.77	137.90	137.41	137.68	137.87	
15	32.30	35.98	36.02	36.03	35.89	35.93	35.88	
16	7.44	8.02	8.17	8.09	7.97	8.07	8.05	
17	21.09	25.08	24.88	25.01	24.87	25.04	24.95	
18	178.86	178.71	178.67	178.56	178.96	178.93	178.82	
19	17.44	16.96	16.90	17.02	16.87	16.88	16.81	
20	15.33	14.47	14.58	14.51	14.59	14.62	14.59	

1'	148.43	143.70	147.98	140.47	147.34	149.64	125.87
2'	107.58	110.36	118.03	130.95	109.81	112.54	111.96
3'	149.17	127.96	125.45	106.92	135.32	126.23	130.50
4'	111.30	113.22*	136.65	149.21	112.90	141.96	151.16
5'	129.39	117.23*	124.37	126.85	129.24	126.23	130.50
6'	119.73	132.23	109.93	116.70	116.56	112.54	111.96
OCH ₃	51.84	51.87	52.12	51.95	51.78	51.79	51.79
C=O							196.15
CH ₃							25.85
CF ₃				124.48	123.97		

Table S3. ^{13}C NMR Spectral data for compounds **28-35** (CDCl_3 , δ , ppm).

C atom	28	29	30	31	32	33	34	35
1	39.03	38.13	38.92	38.05	38.95	38.04	38.89	38.01
2	18.21	18.10	17.96	18.19	17.94	18.10	18.06	18.07
3	36.12	36.46	36.67	36.43	36.58	36.85	36.84	36.85
4	47.40	47.33	46.38	47.14	46.37	47.23	46.34	47.20
5	43.54	43.79	44.65	42.57	44.81	47.49	44.80	47.50
6	26.87	28.58	24.87	30.75	24.87	32.61	24.86	32.62
7	43.97	45.34	123.88	79.60	124.51	56.17	124.24	56.01
8	132.55	136.08	135.91	134.71	135.32	131.13	135.61	131.17
9	51.37	48.28	47.48	46.80	47.64	49.85	47.49	49.86
10	36.91	38.01	34.95	37.73	34.96	37.87	34.89	37.84
11	19.18	18.69	19.60	18.31	19.53	18.90	19.44	18.89
12	32.99	33.08	31.83	32.97	31.54	32.96	31.40	32.84
13	34.73	34.39	36.55	34.13	36.48	33.85	36.25	33.85
14	138.21	136.65	63.52	137.05	63.19	134.25	62.29	134.10
15	36.12	36.21	32.42	36.28	32.30	36.24	32.28	36.26
16	8.31	8.42	7.48	8.27	7.46	8.05	7.45	8.09
17	25.94	25.57	21.12	25.34	21.16	25.60	21.10	25.62
18	178.65	178.89	178.88	179.03	178.86	178.96	178.92	178.94
19	16.96	17.04	17.55	16.95	17.48	17.03	17.01	17.01
20	15.49	15.18	15.38	14.50	15.32	15.08	14.69	15.07

1'	135.94	135.99	144.61	144.04	147.92	148.07	150.19	150.40
2'	140.44	131.25	110.86	109.29	110.37	108.75	112.75	126.42
3'	110.08	109.34	128.01	128.30	137.30	135.95	126.34	111.92
4'	129.59	141.47	113.30*	115.71	113.07	113.10	141.25	138.43
5'	118.29	115.21	117.10*	119.37	129.25	129.33	126.32	126.42
6'	127.59	127.15	132.23	132.55	116.99	116.04	112.75	111.92
OCH ₃	52.26	51.98	51.80	51.75	51.80	51.11	51.83	52.12
<u>CF₃</u>				123.29	125.85	123.69	118.02	

Table S4. ¹³C NMR Spectral data for compounds **36, 38-40, 42, 44, 45** (CDCl₃, δ, ppm).

C atom	36	38	39	40	42	44	45
1	38.77	38.13	38.48	38.01	38.25	38.28	41.25
2	17.87	17.99	18.23	18.05	17.99	18.06	18.05
3	36.60*	36.97	36.20	36.90	36.80	37.03	37.68
4	46.30	47.19	47.36	46.91	46.71	47.76	47.02
5	44.75	46.98	42.63	43.77	42.67	47.05	42.18
6	24.86	28.85	31.51	29.35	30.66	29.09	32.99
7	124.20	61.68	73.30	56.07	57.21	51.83	53.97
8	135.76	130.95	134.88	133.35	133.89	134.81	134.36
9	47.52	50.26	46.73	47.42	47.60	50.08	46.65
10	36.63	37.24	37.91	37.85	37.42	37.48	38.01

11	19.31	18.90	18.29	18.89	18.18	18.43	18.33
12	31.20	32.44	36.55	32.51	32.85	33.45	36.92
13	32.24	34.04	34.08	33.95	33.74	34.09	35.92
14	62.21	131.96	136.36	131.57	137.63	137.34	136.02
15	35.00	36.10	33.18	36.27	35.40	35.85	33.94
16	7.43	8.15	8.39	8.12	7.89	8.12	8.11
17	21.00	26.06	25.34	25.53	24.66	28.48	25.17
18	178.81	178.77	179.18	178.77	178.65	178.70	179.07
19	17.41	17.07	17.07	17.04	16.84	16.65	16.79
20	15.24	15.27	14.23	15.11	14.60	14.50	14.22
1'	125.96	154.96		153.08	140.75		
2'	111.98	110.76		111.74	127.06		
3'	130.69	126.09		126.37	128.80		
4'	151.69	136.80		137.43	132.20		
5'	130.69	126.09		126.37	128.80		
OCH ₃ NCH ₃ CH ₃ <u>C(CH₃)₃</u> NHC(O)O C=O	6'	111.98	110.76	111.74	127.06		
		51.85	52.17	52.05	52.15	52.19	51.97
			33.46				52.15
						28.44	
						78.84	
						160.25	
<hr/>							
							196.08

S2. X-ray crystal structure analysis for compounds 5, 24, 27, and 36

The compounds **24**, **27** crystallizes in the orthorhombic space groups $P2_12_12_1$, while **5**, **36** crystallizes in the monoclinic $P2_1$ group. The crystallographic data are listed in Table S5. Molecular structure of compounds **6**, **24**, **27**, **36** is illustrated in Fig. 2. The obtained crystal structures were analyzed for short contacts between non-bonded atoms using PLATON [26] and MERCURY programs [27]. CCDC 1407201 (**5**), 1407203 (**24**), 1407202 (**27**), 1422327 (**36**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Table S5. XRD data for compounds **5**, **24**, **27** and **36**

Compound	5	27	24	36
Empirical formula	$C_{21}H_{32}O_2$	$C_{29}H_{41}NO_3$	$C_{28}H_{40}N_2O_5$	$C_{29}H_{41}NO_3$
Formula weight	316.47	451.63	484.62	451.63
Temperature K	200(2)	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
Unit cell dimensions $a \text{ \AA}$	6.3192(2)	9.3376(4)	9.5312(3)	8.0363(3)
$b \text{ \AA}$	12.2161(5)	9.4039(4)	32.961(1)	23.4011(9)
$c \text{ \AA}$	12.2957(5)	30.190(1)	8.2760(4)	13.8684(6)
α°	90.00	90	90	90
β°	104.082(2)	90	90	95.380(2)
γ°	90	90	90	90
Volume \AA^3	920.65(6)	2650.98(19)	2600.0(2)	2596.6(2)
Z	2	4	4	4
Density (calcd.) Mg.m^{-3}	1.142	1.132	1.238	1.155
Abs. coefficient mm^{-1}	0.071	0.072	0.084	0.073
F(000)	348	984	1048	984
Crystal size mm^3	0.8 x 0.4 x 0.04	0.5 x 0.5 x 0.80	0.50 x 0.30 x 0.20	0.40 x 0.30 x 0.20
Θ range for data collection $^\circ$	1.7 – 27.5	1.4 – 26.0	1.2 - 25.7	1.5 – 26.1
Index ranges	-8 ≤ h ≤ 8, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15	-11 ≤ h ≤ 11, -11 ≤ k ≤ 9, -34 ≤ l ≤ 37	-11 ≤ h ≤ 11, -40 ≤ k ≤ 40, -10 ≤ l ≤ 10	-9 ≤ h ≤ 9, -28 ≤ k ≤ 28, -17 ≤ l ≤ 17
Reflections collected	27580	25551	28442	51381
Independent reflections	4235 R(int) = 0.034	5153 R(int) = 0.043	4959 R(int) = 0.064	10224 R(int) = 0.050
Completeness to θ %	100.0	98.8	100.0	99.8
Data / restraints/ parameters	4235 / 1 / 213	5153 / 0 / 304	4959 / 0 / 322	10224 / 1 / 607
Goodness-of-fit on F^2	1.15	1.06	1.12	1.06
Final R indices $ I > 2\sigma(I)$	$R_1 = 0.0444$, $wR_2 = 0.1439$	$R_1 = 0.0537$, $wR_2 = 0.1498$	$R_1 = 0.0384$, $wR_2 = 0.1012$	$R_1 = 0.0444$, $wR_2 = 0.1150$
Final R indices (all data)	$R_1 = 0.0467$, $wR_2 = 0.1488$	$R_1 = 0.0739$, $wR_2 = 0.1685$	$R_1 = 0.0536$, $wR_2 = 0.1204$	$R_1 = 0.0639$, $wR_2 = 0.1383$
Largest diff. peak / hole e.\AA^{-3}	0.22/ -0.23	0.44/ -0.22	0.20 / -0.28	0.21 / -0.18

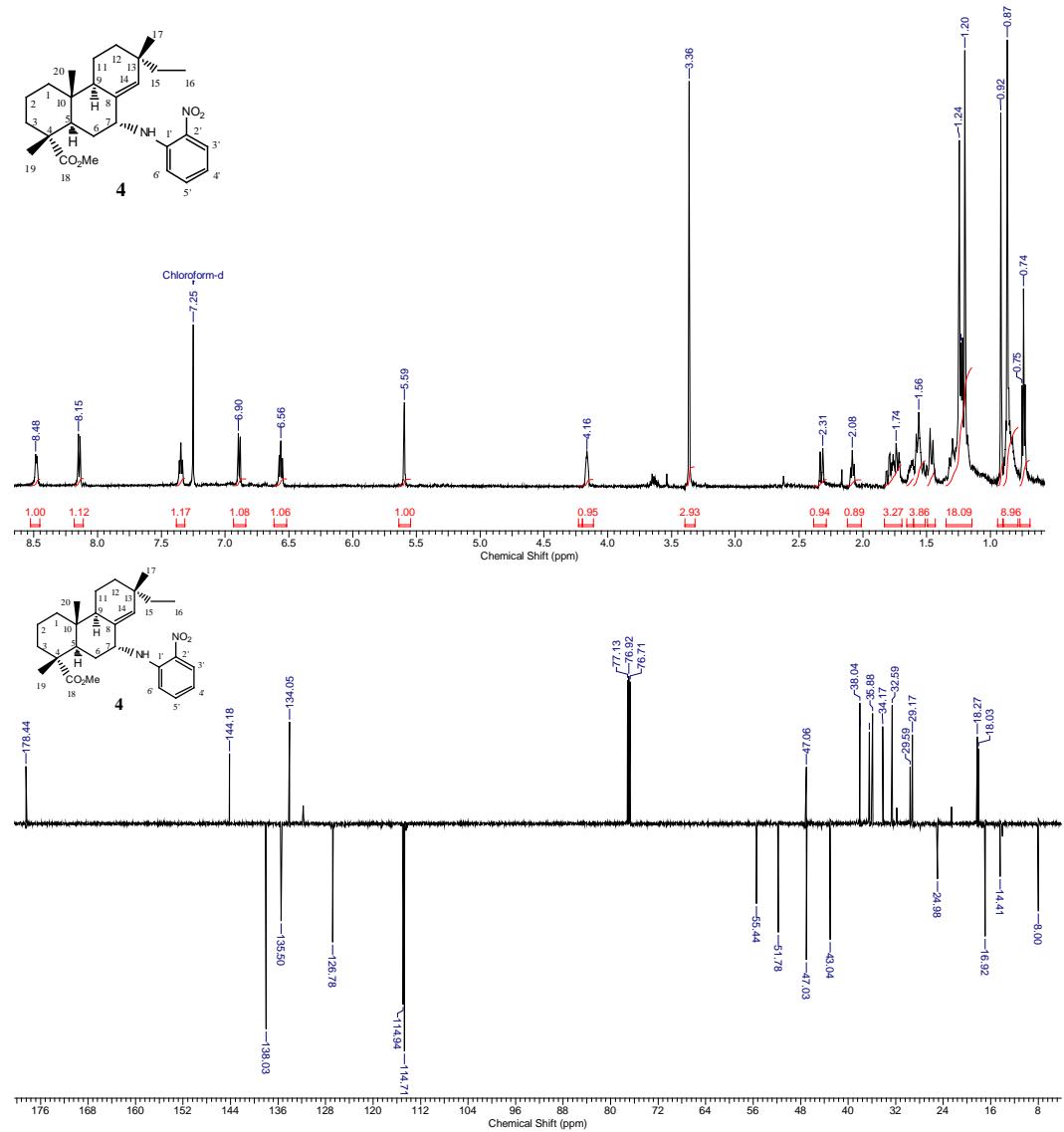
Table S6. Parameters of the short inter-molecular and the selected intra-molecular contacts.

Compound 5			Compound 27			
Type interaction	Short contact	Value, Å	Type interaction	Short contact	Value, Å	
<i>intra</i>	O1...H4	2.41	intra	N1...H5	2.55	
<i>intra</i>	O1...H9	2.39	H-bond			
<i>intra</i>	O2...H3	2.55	<i>D-H...A</i>	D-H, Å	H...A, Å	D...A, Å
<i>intra</i>	O2...H31	2.47	N1-H...O3	0.86	2.37	3.220(3)
			C8'-H...O2	0.96	2.49	3.350(4)
			C11-H...O2	0.97	2.55	3.487(4)
Compound 24			Compound 36			
Type interaction	Short contact	Value, Å	Type interaction	Short contact	Value, Å	
<i>inter</i>	O2...H15b	2.61	<i>inter</i>	O1a...H43	2.54	
<i>inter</i>	O3...H14	2.63	<i>inter</i>	O2a...H50	2.57	
<i>inter</i>	O5...H16a	2.65	H-bond			
<i>intra</i>	O3...N1	2.613(2)	<i>D-H...A</i>	D-H, Å	H...A, Å	D...A, Å
<i>intra</i>	N1...N2	2.933(2)	N1b-H...O2a	0.86	2.53	3.280(3)
<i>intra</i>	N1...H5	2.66	N1a-H...O3b	0.86	2.30	3.145(3)
Note, that normal O..H, N...H and N...N contacts are 2.68, 2.74 and 3.27 Å correspondingly [Rowland R.S. and Taylor R. // J. Phys. Chem. – 1996. – 100 . – P. 7384].						

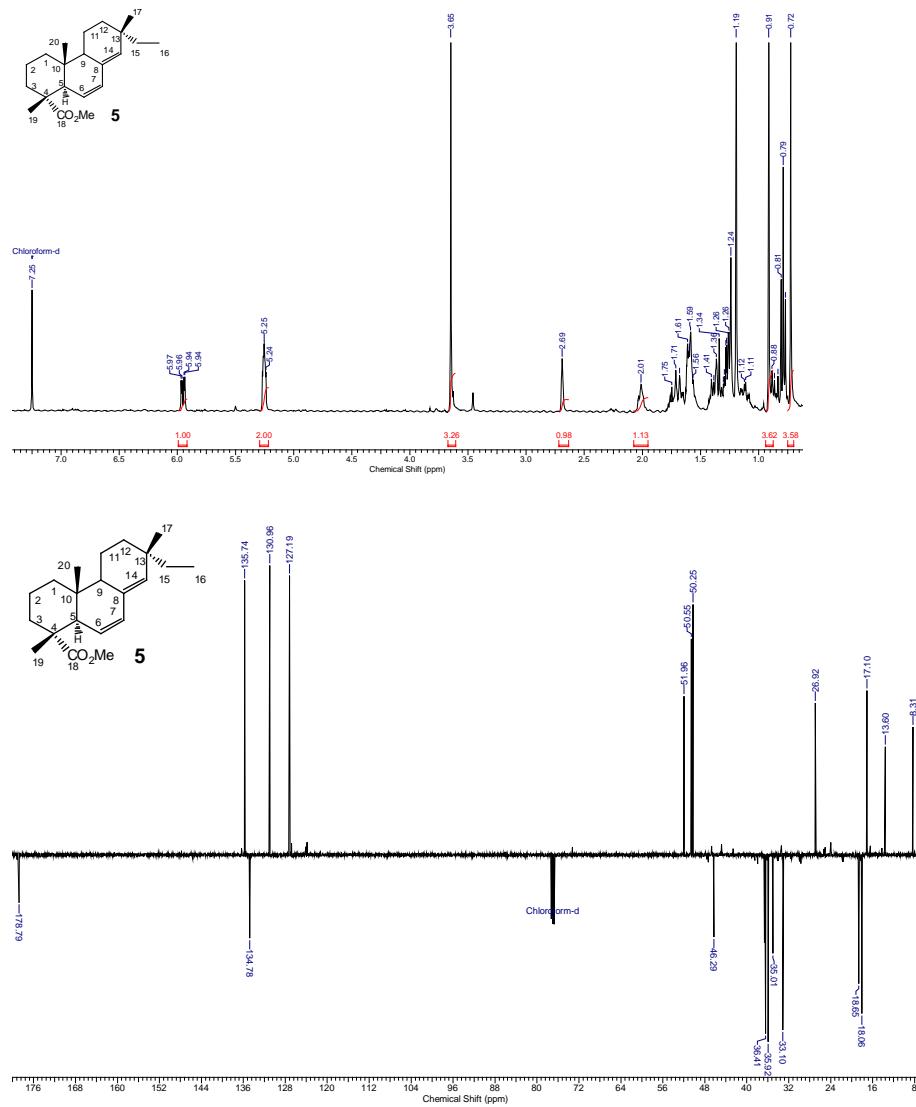
S3. ^1H and ^{13}C spectra of synthesized compounds

1. ^1H and ^{13}C spectra of compound **4**
2. ^1H and ^{13}C spectra of compound **5**
3. ^1H and ^{13}C spectra of compound **6**
4. ^1H and ^{13}C spectra of compound **7**
5. ^1H and ^{13}C spectra of compound **10**
6. ^1H and ^{13}C spectra of compound **12**
7. ^1H and ^{13}C spectra of compound **13**
8. ^1H and ^{13}C spectra of compound **15**
9. ^1H and ^{13}C spectra of compound **22**
10. ^1H and ^{13}C spectra of compound **23**
11. ^1H and ^{13}C spectra of compound **24**
12. ^1H and ^{13}C spectra of compound **25**
13. ^1H and ^{13}C spectra of compound **27**
14. ^1H and ^{13}C spectra of compound **29**
15. ^1H and ^{13}C spectra of compound **30**
16. ^{13}C spectra of compound **31**
17. ^1H and ^{13}C spectra of compound **33**
18. ^1H and ^{13}C spectra of compound **35**
19. ^1H and ^{13}C spectra of compound **38**
20. ^{13}C spectra of compound **39**
21. ^1H and ^{13}C spectra of compound **42**

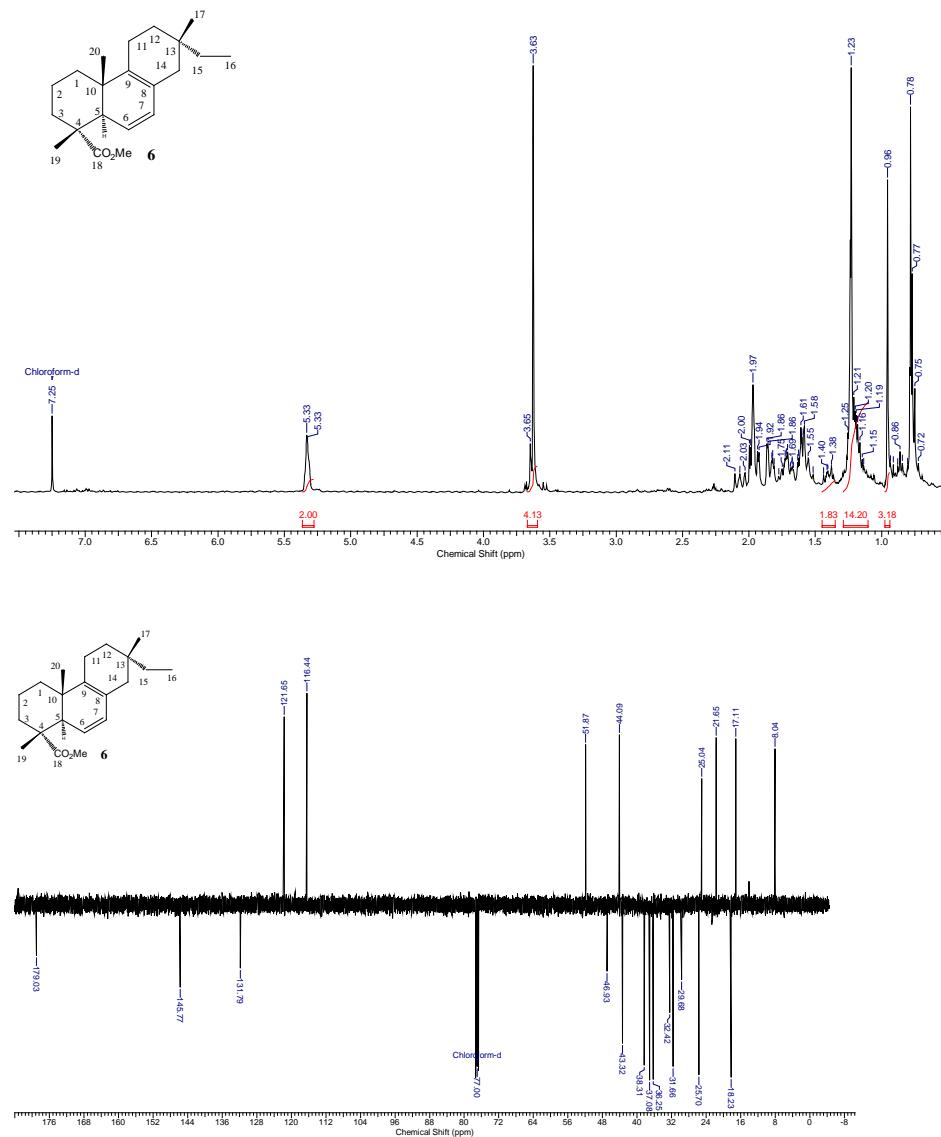
Compound 4



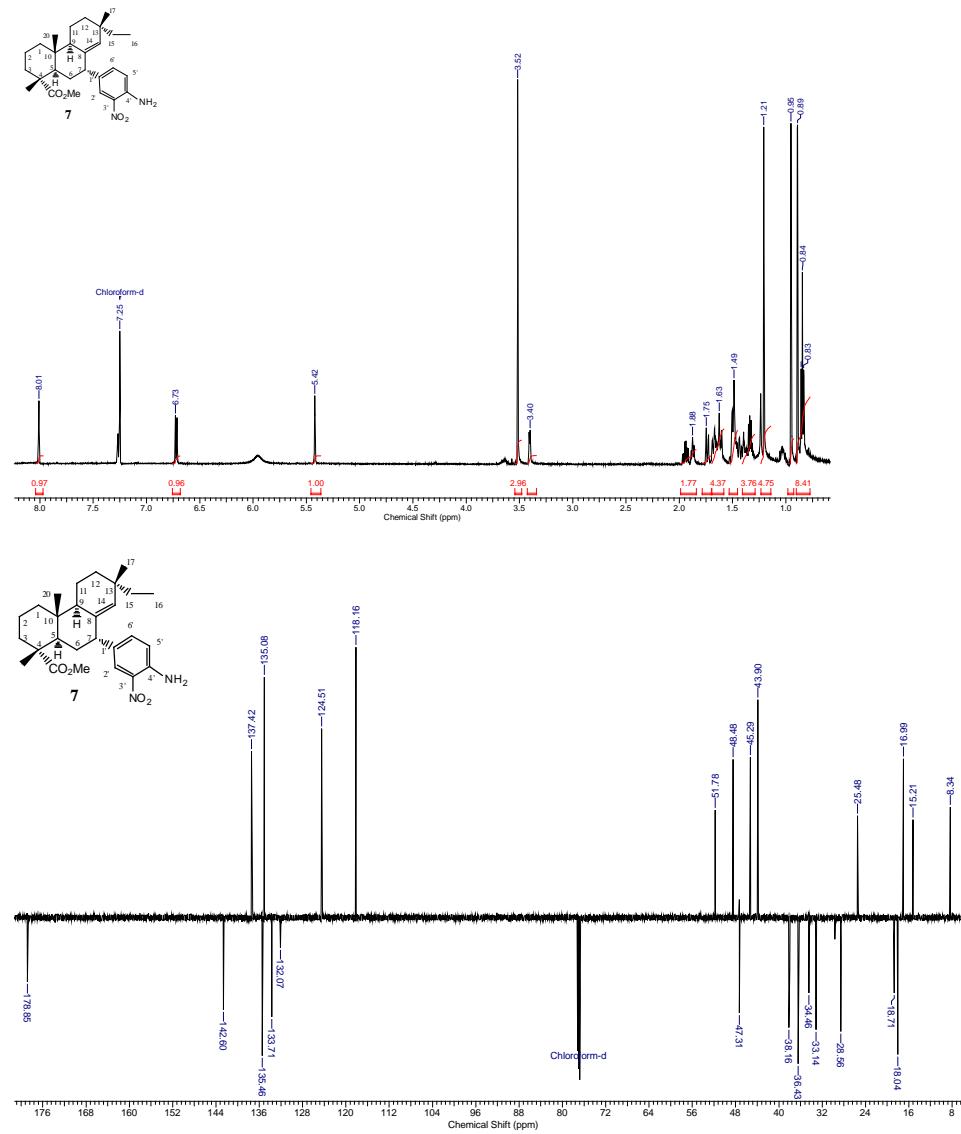
Compound 5



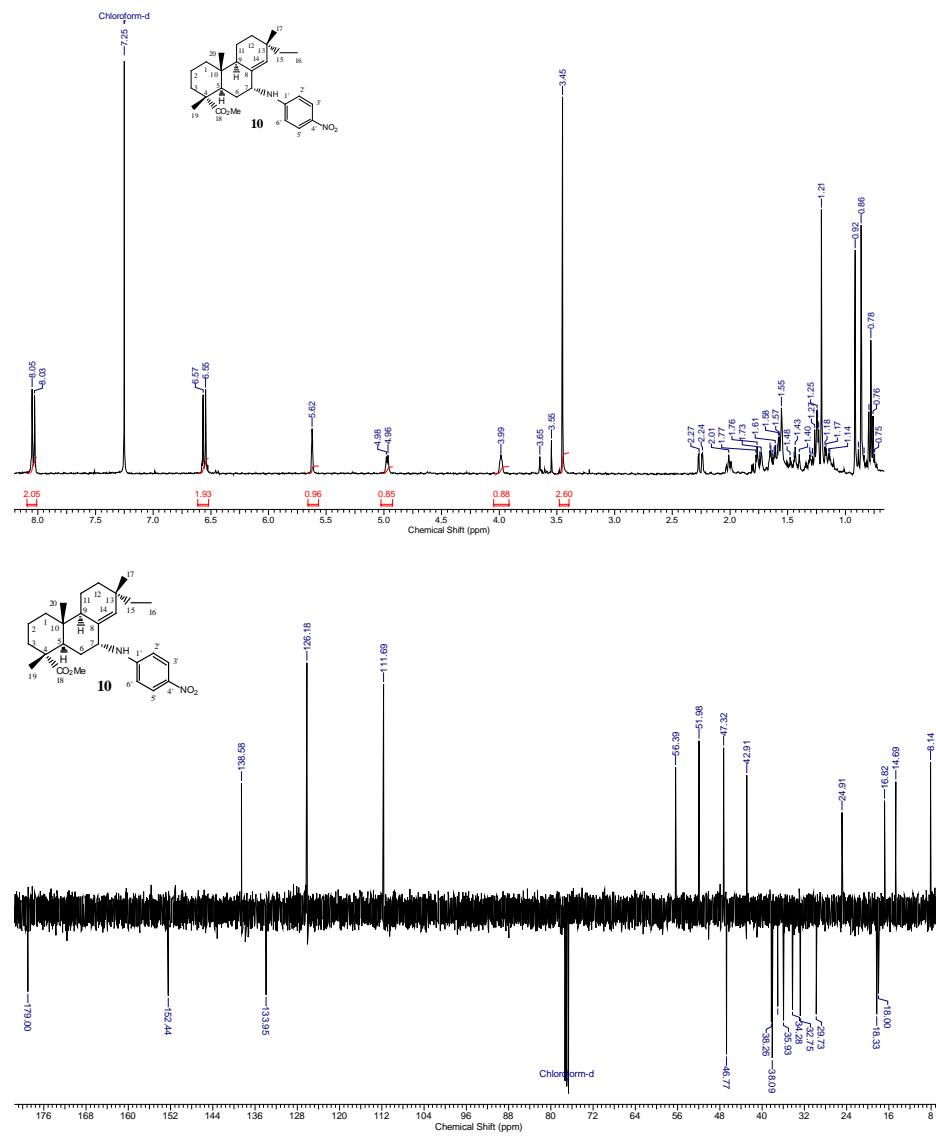
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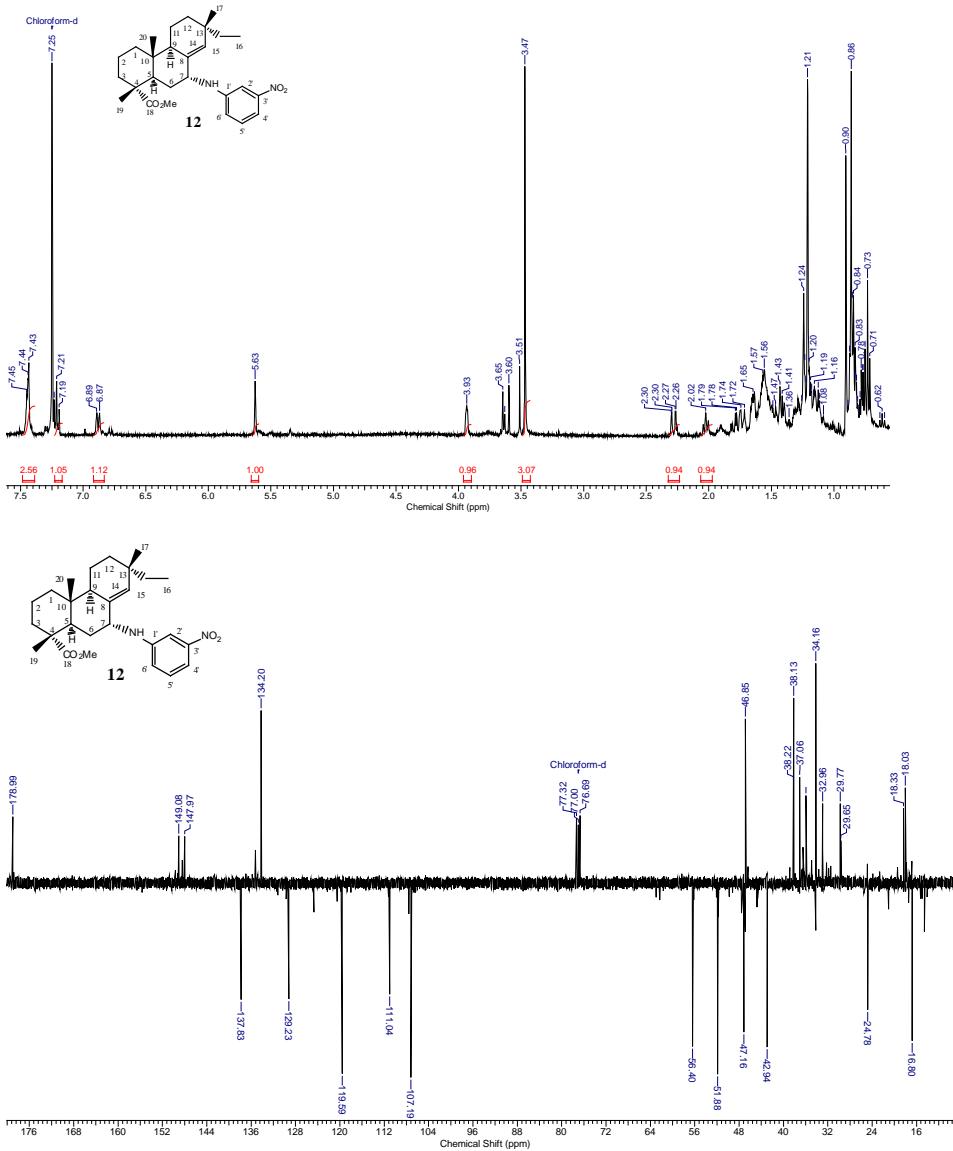
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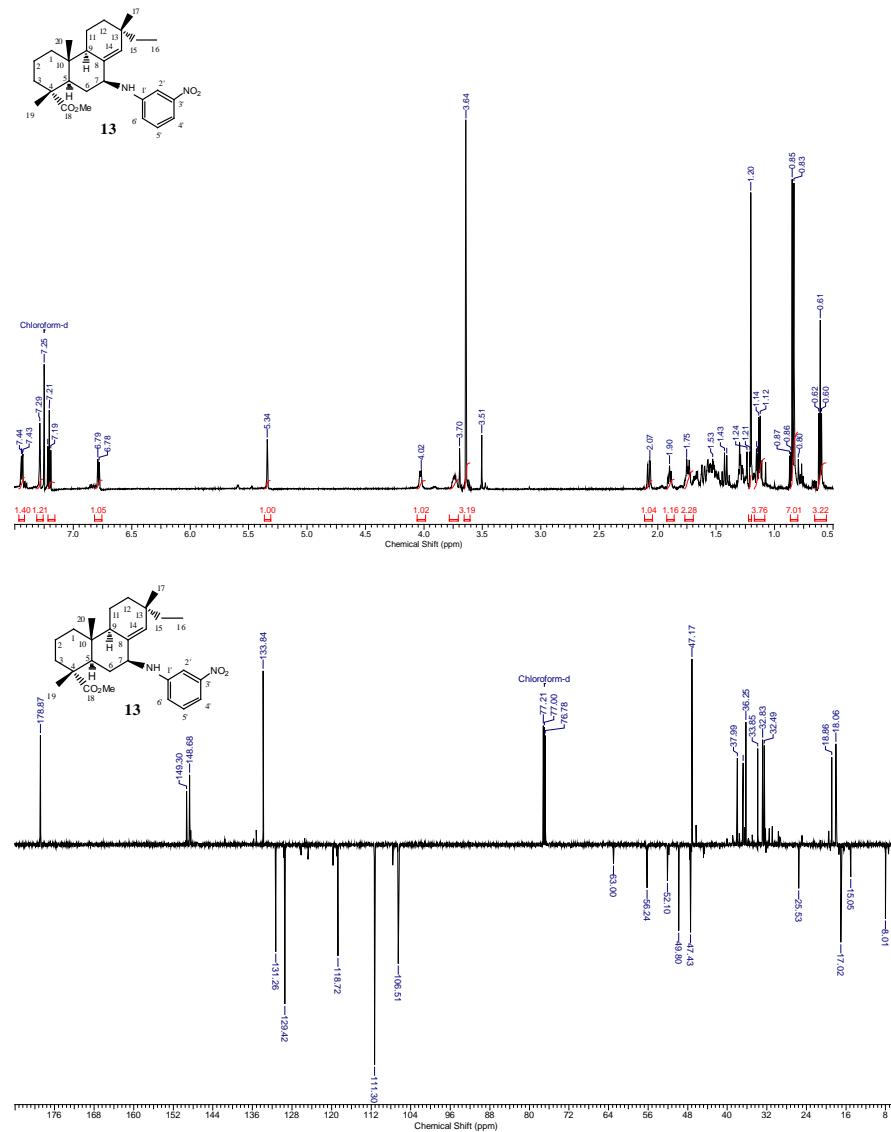
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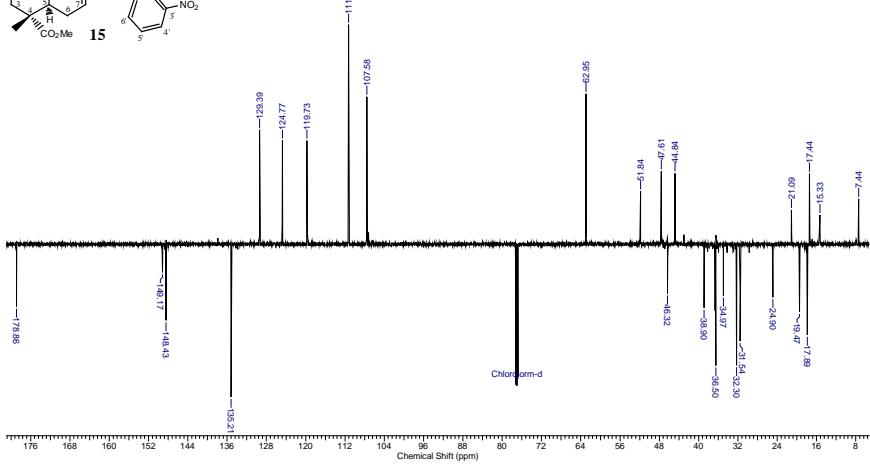
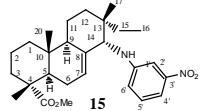
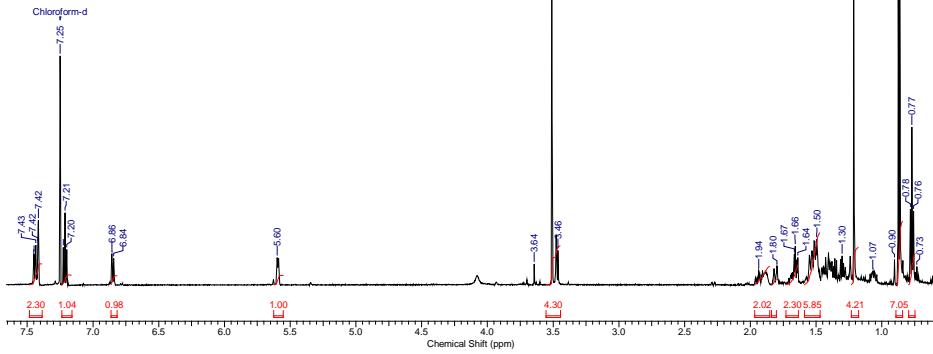
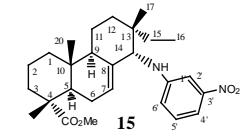
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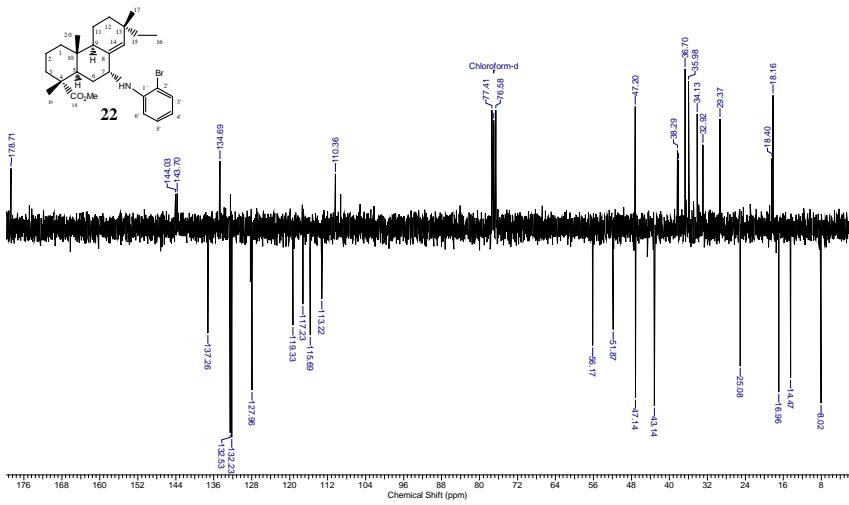
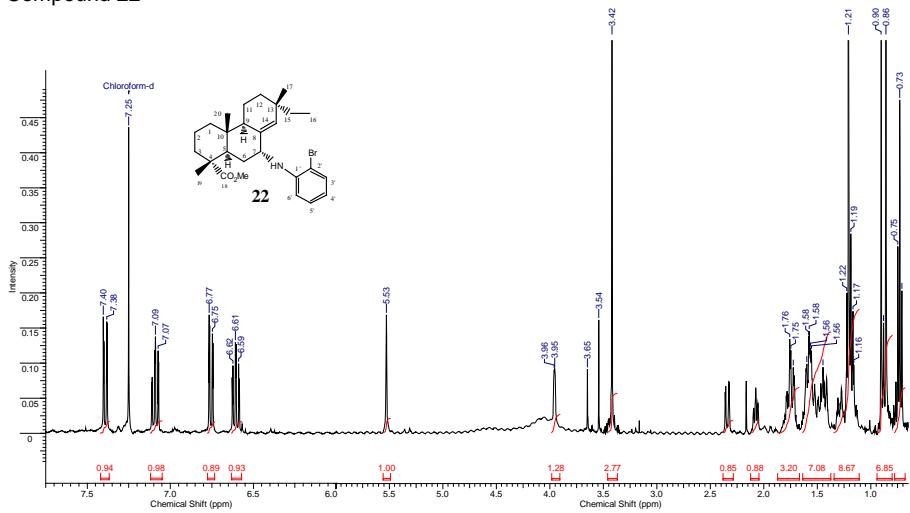
Compound 13



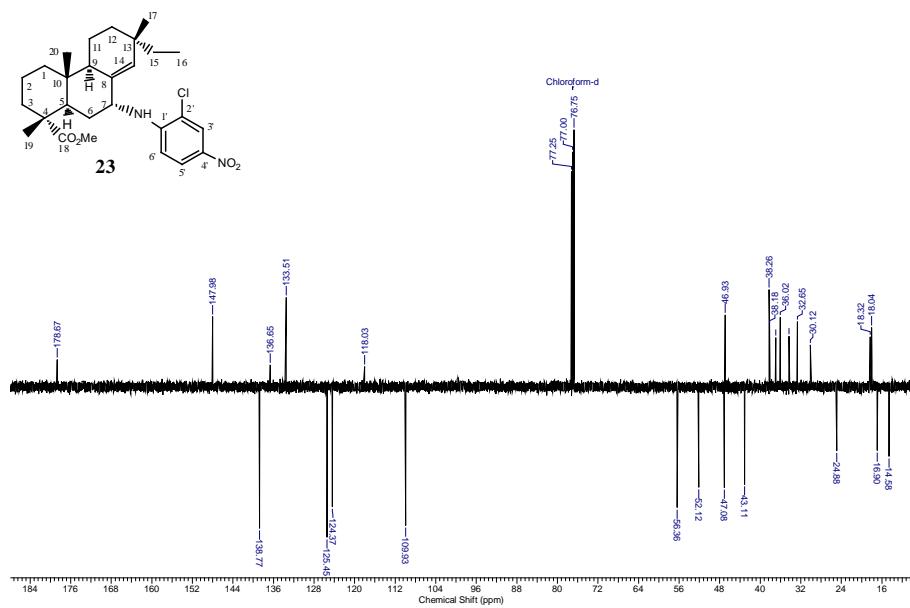
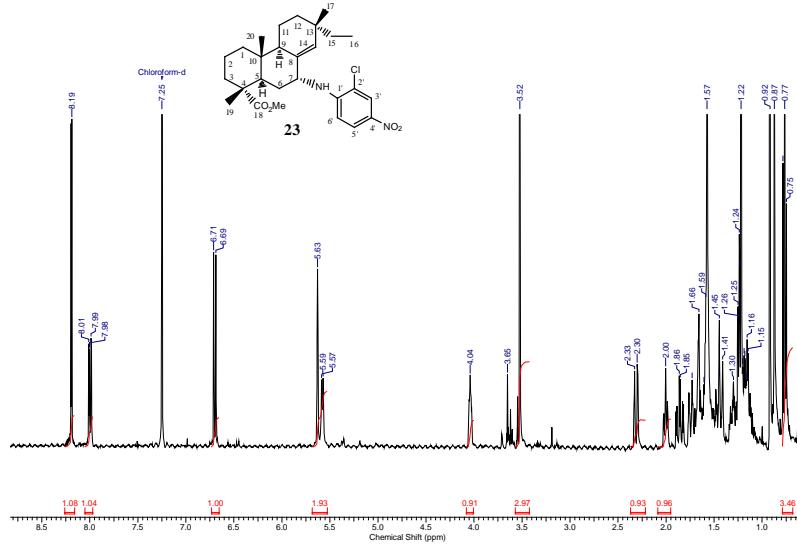
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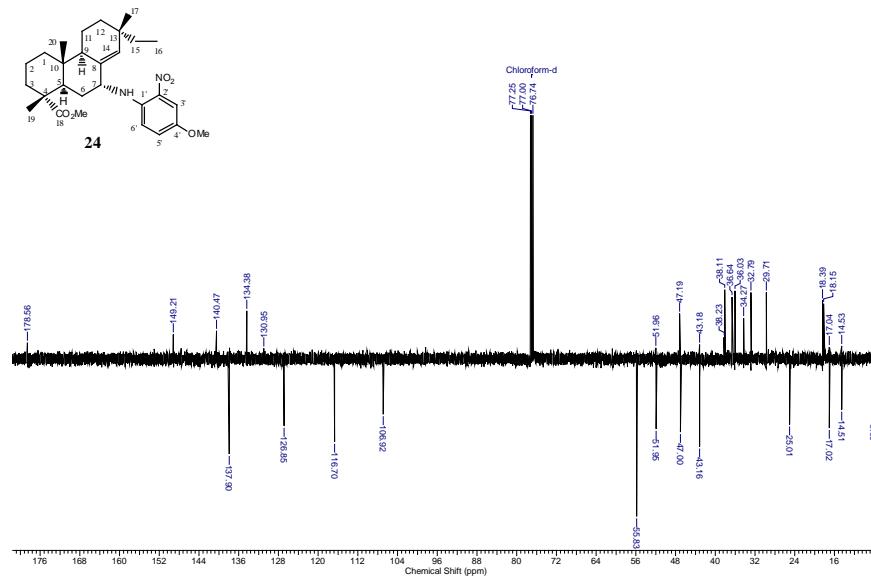
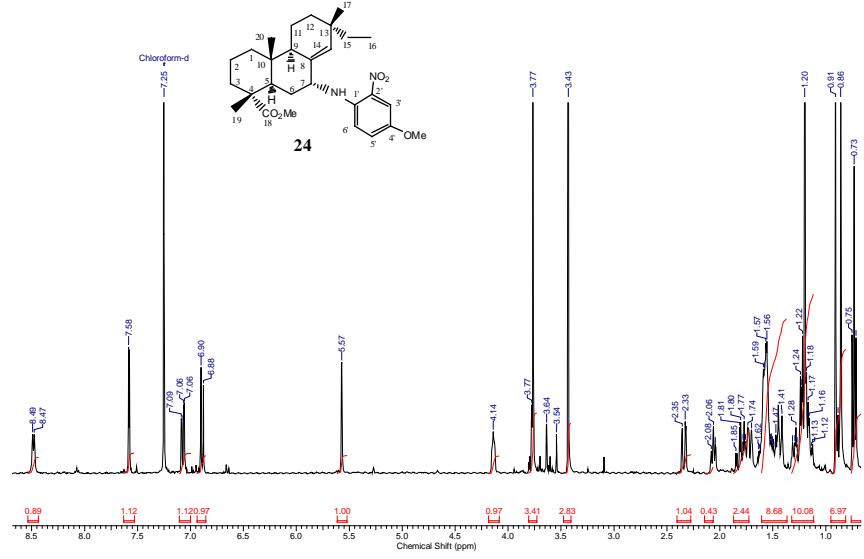
Compound 22



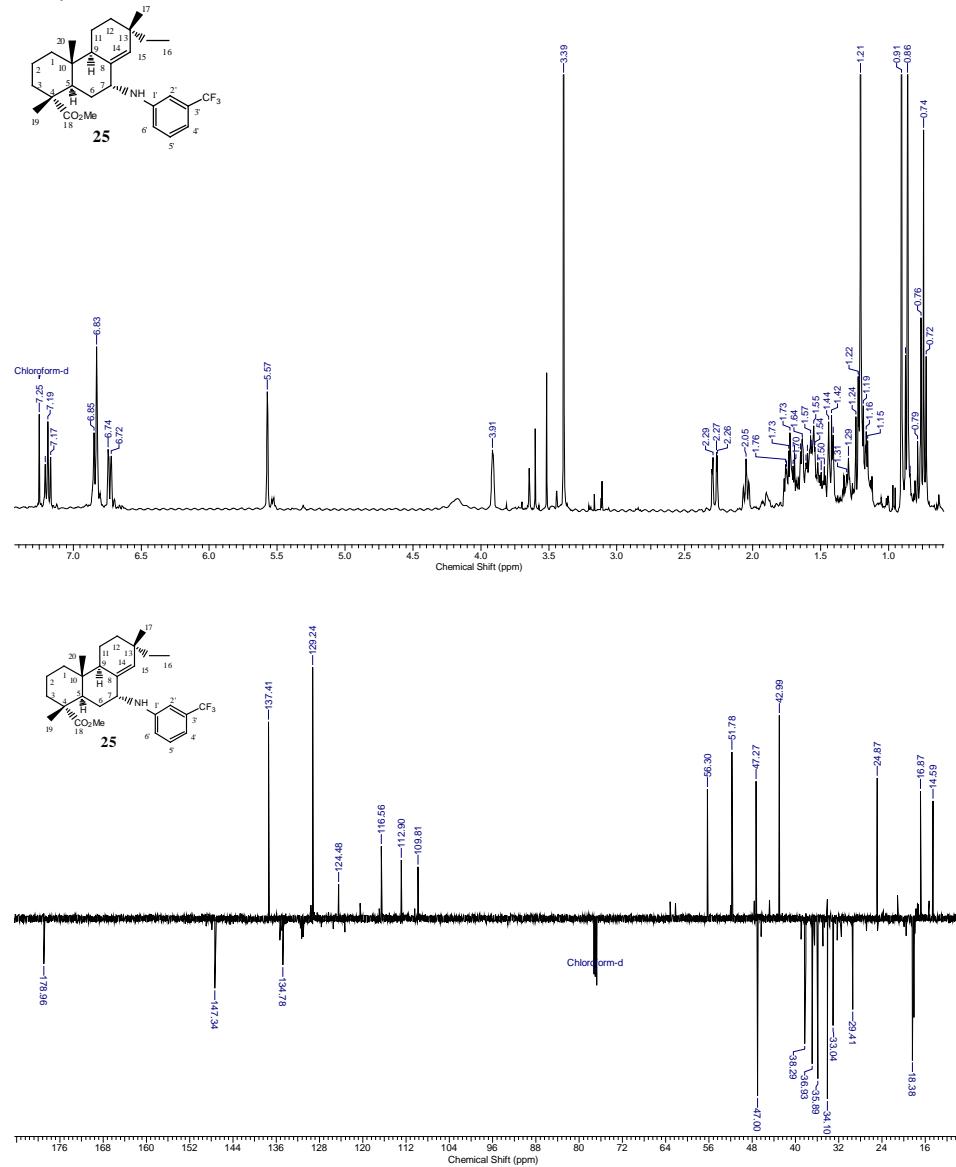
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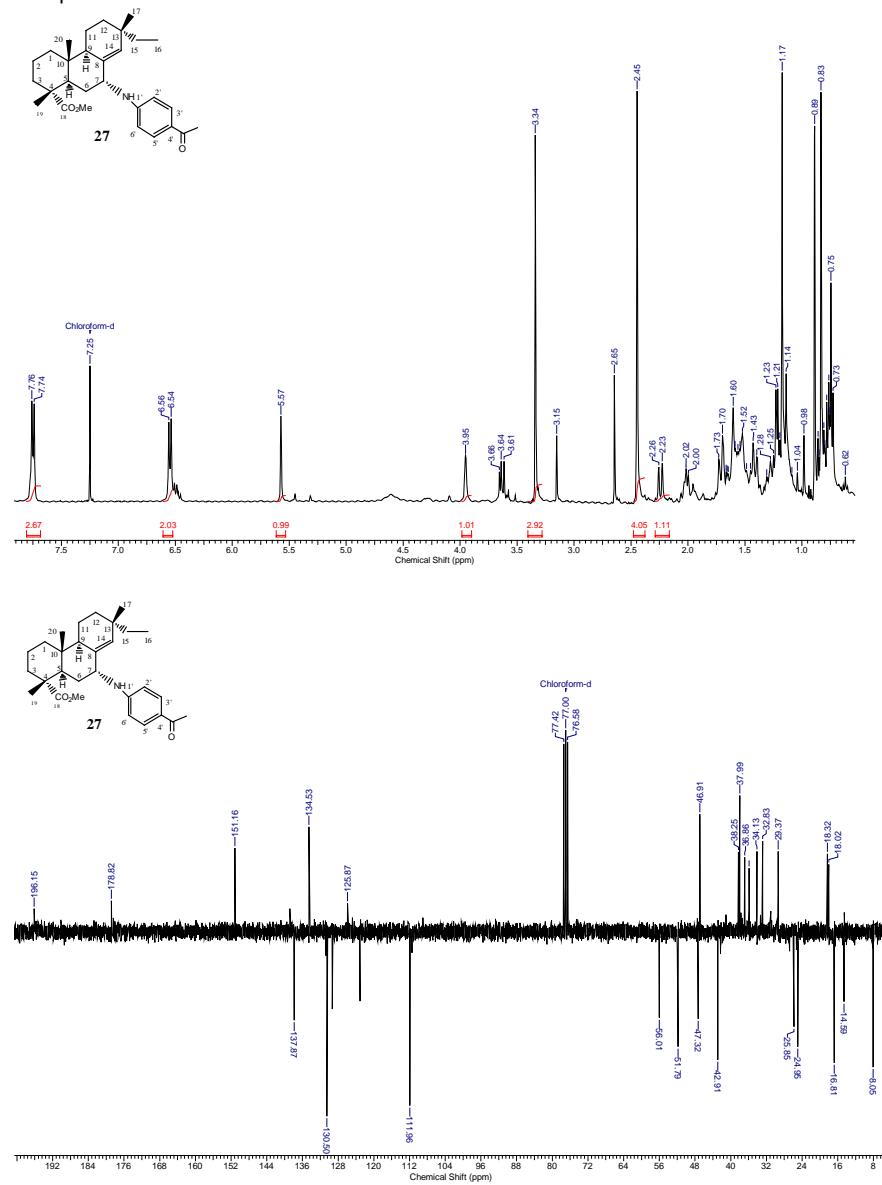
Compound 24



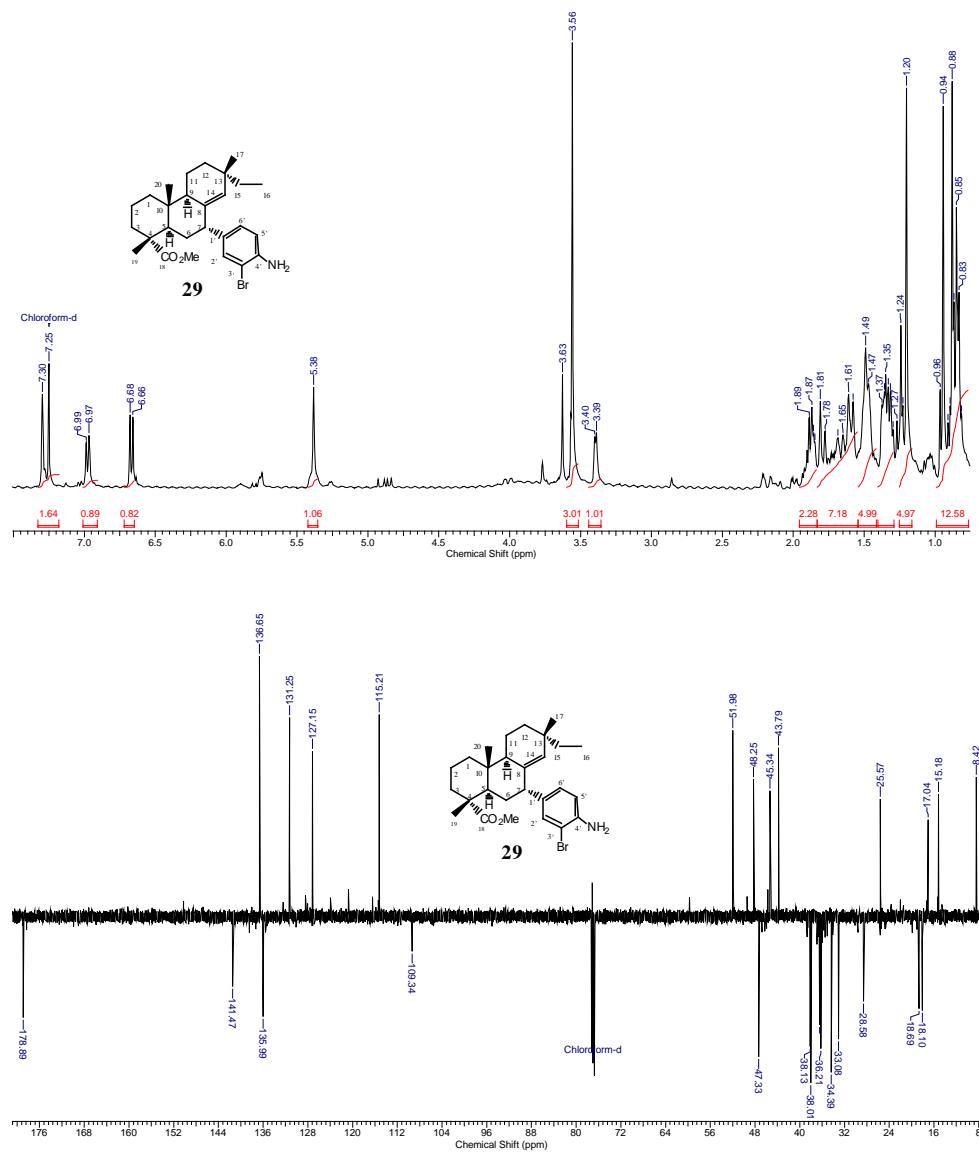
Compound 25



Compound 27

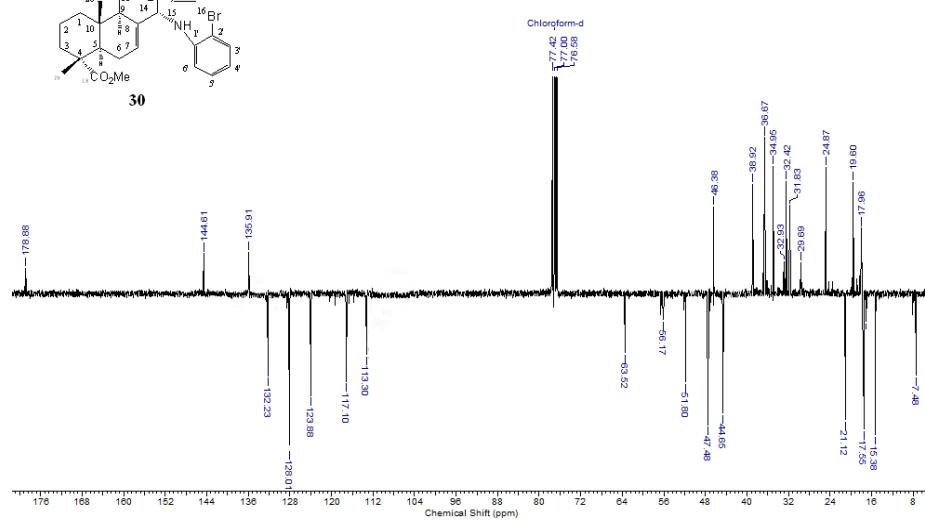
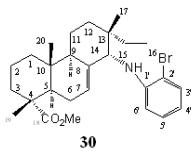
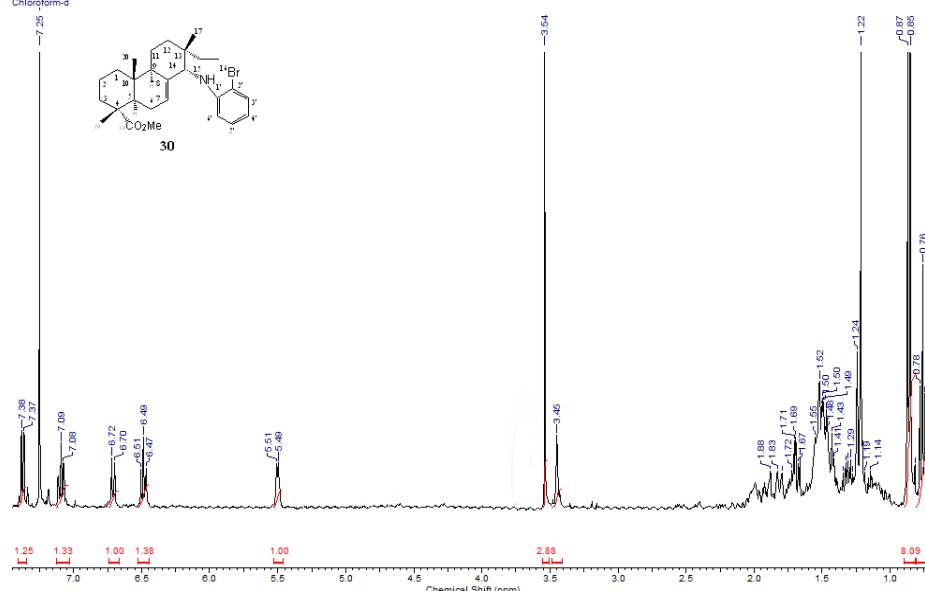
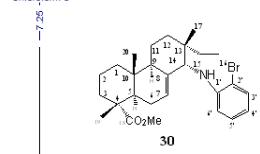


Compound 29

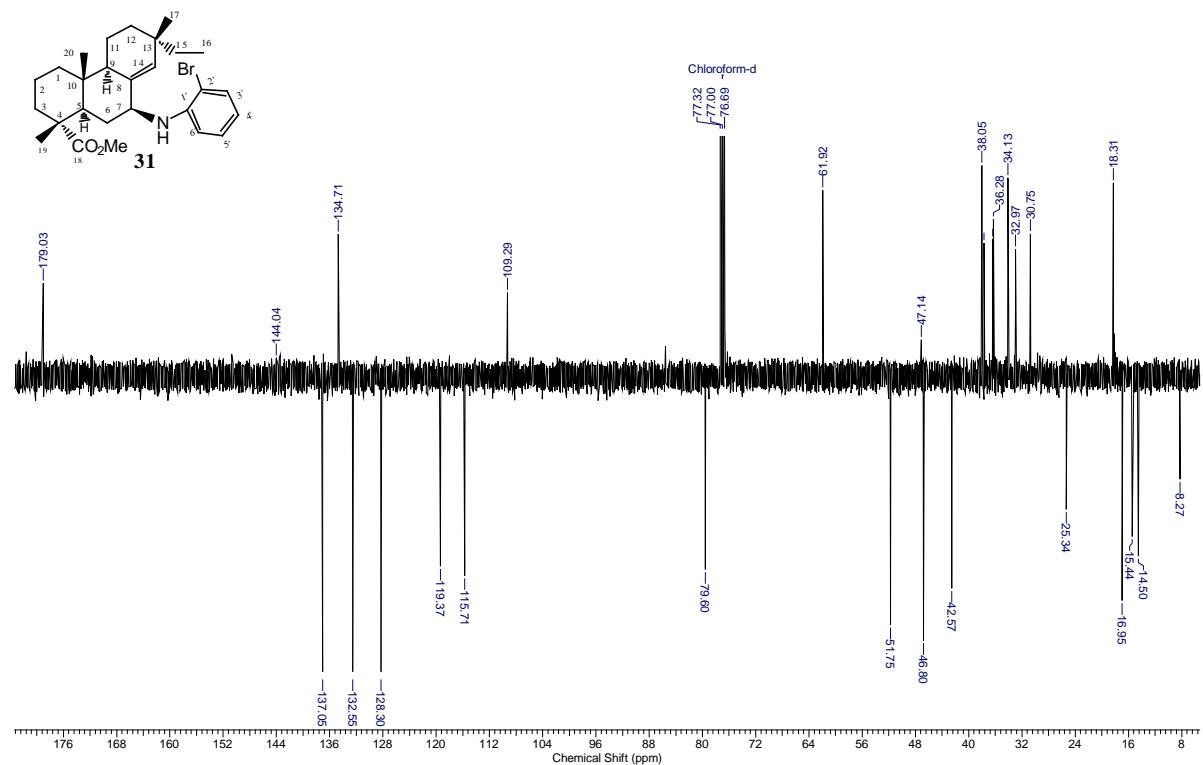


Compound 30

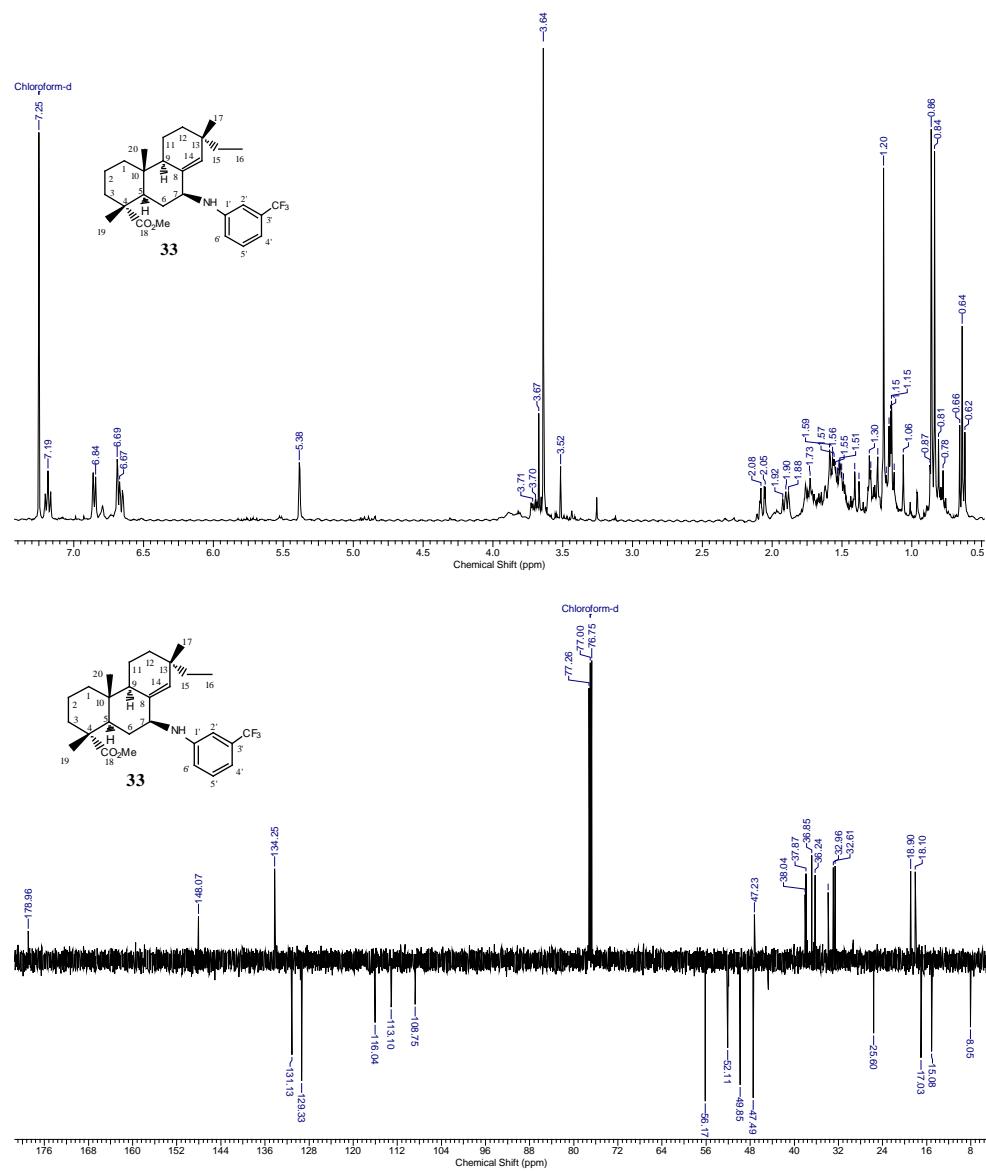
Chloroform-d



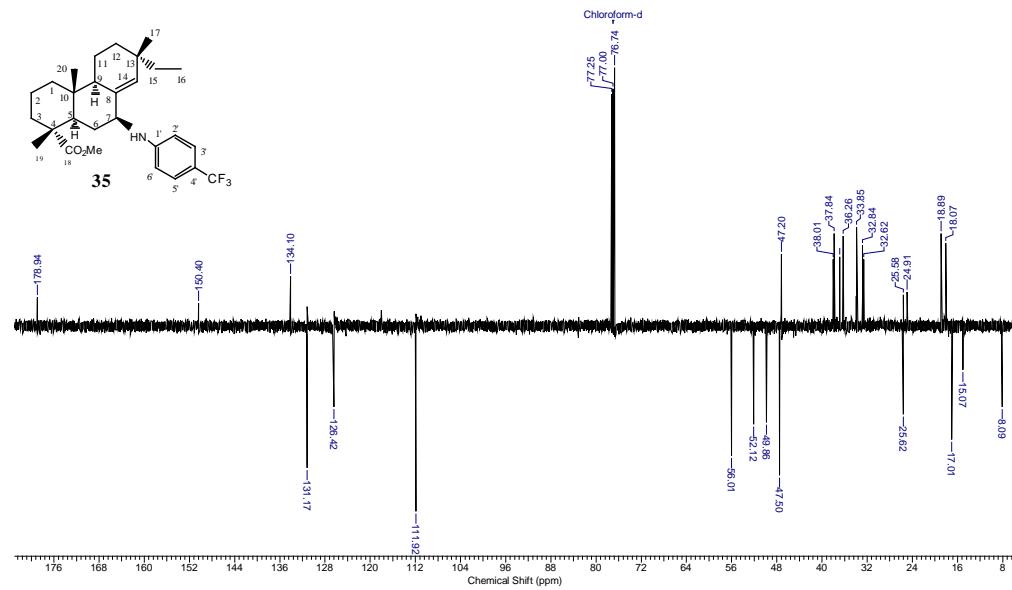
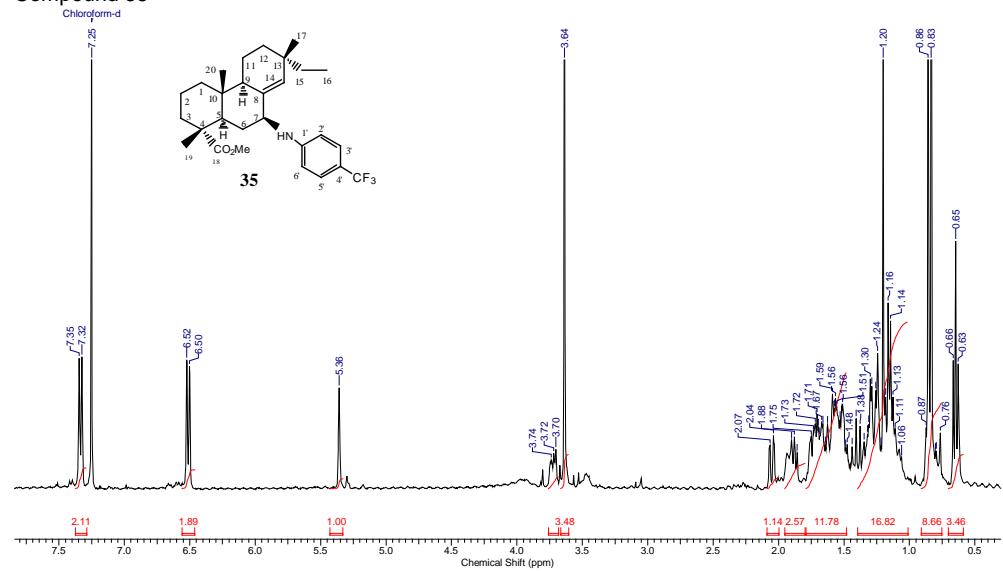
Compound 31



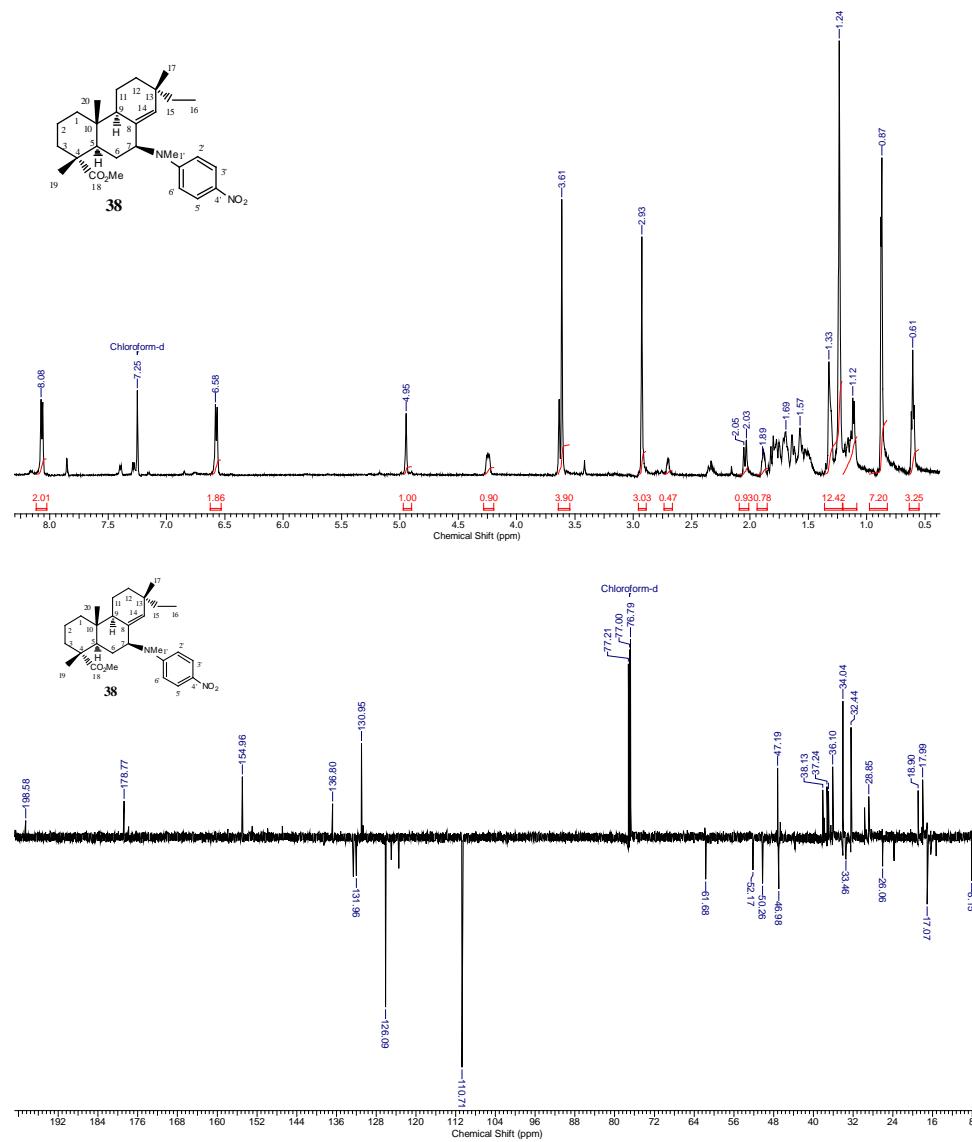
Compound 33



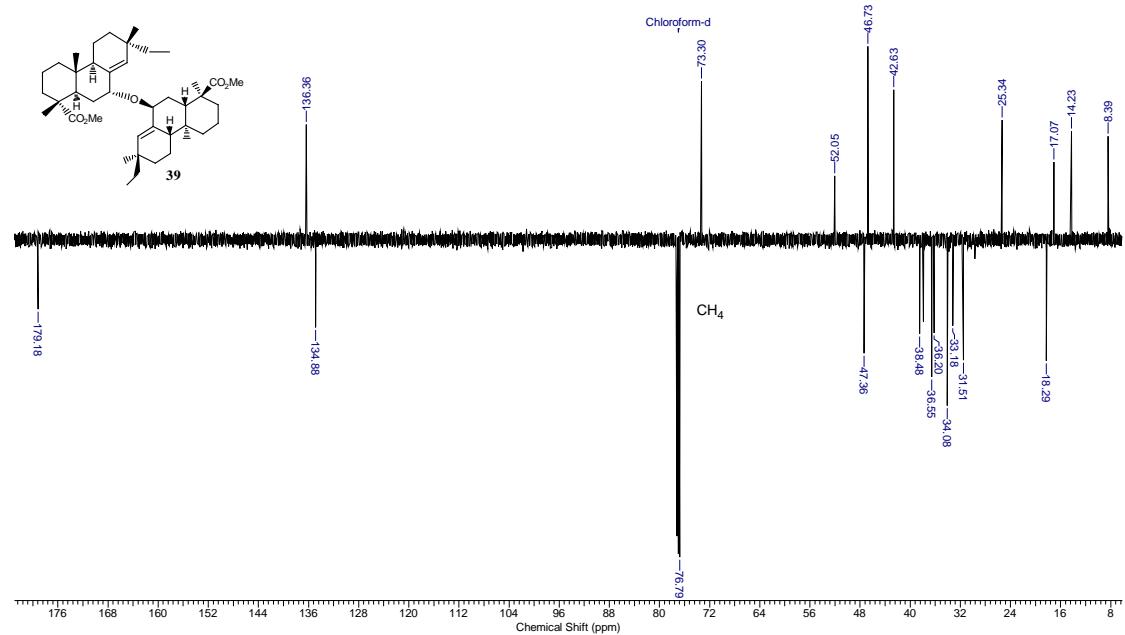
Compound 35



Compound 38



Compound 39



Compound 42

